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COMPONENTS OF THE BARK OF *PRUNUS PUDDUM**

Part III. Synthesis of Padmakastein and its Derivatives

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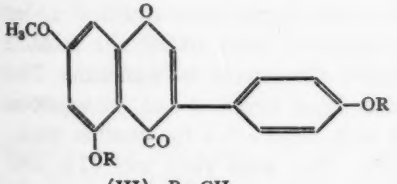
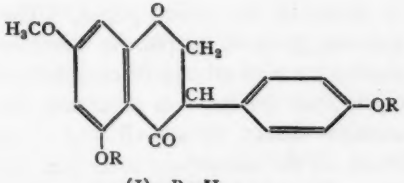
Received June 23, 1958

Padmakastein (I)[1] was the first isoflavanone to be isolated from plant materials. Its constitution was based mainly on the dehydrogenation of the complete methyl ether (II) by means of selenium dioxide to yield prunetin dimethyl ether (III) and of the acetate (IV) to prunetin diacetate (V). It was also reported that prunetin (VI) could be reduced by means of sodium meta-bisulphite to give padmakastein (I). Later experiments carried out in this laboratory have shown that sodium hydrosulphite and sodium meta-bisulphite are not suitable for reducing isoflavones. Prunetin (VI) is unaffected when a weakly basic medium (aqueous alcoholic sodium carbonate) is employed. In strongly alkaline solution (aqueous sodium hydroxide) a product is obtained which has melting point, colour reactions and analytical values somewhat near those of the isoflavanone (I). But the difference was noted when its derivatives were prepared and it could now be identified as 2: 6: 4′-trihydroxy-4-methoxy desoxybenzoin arising out of the fission of the isoflavone.



(III) R=CH_3
(V) R=$COCH_3$
(VI) R=H



(I) R=H
(II) R=CH_3
(IV) R=$COCH_3$

Other methods of reduction were therefore attempted. Catalytic hydrogenation using platinum oxide catalyst was reported by Robertson *et al.*[2] to carry the reduction of santal methyl ether too far, affecting the carbonyl group also. But by suitably restricting the time, Bradbury and White[3]

* Part II. Narasimhachari and Seshadri, *Proc. Ind. Acad. Sci.*, 1952, **35 A**, 202.

succeeded in reducing prunetin dimethyl ether (III) to the dihydro derivative (II). But the palladised charcoal catalyst employed by King and his co-workers[4–6] for isoflavones appeared to be better and we used it for the reduction of prunetin dimethyl ether (III) quite satisfactorily. The work was completed in 1956 but owing to lack of the natural sample for comparison it was not published. Meanwhile Gilbert *et al.*[7] in connection with their work on iso-shekkangenin also reduced prunetin dimethyl ether (III) in this way.

This method of reduction has also been applied for the synthesis of padmakastein (I) itself. Prunetin diacetate (V) was subjected to this reduction and the dihydro compound (IV) (padmakastein diacetate) was deacetylated with alcoholic hydrochloric acid. The product agreed with padmakastein (I) in every respect. Comparison was also made between the acetates and the methyl ethers of the natural and synthetic compounds.

For the above mentioned comparison a fresh sample of padmakastein (I) was obtained from the bark of *Prunus puddum* using a modified procedure. In the course of this work it was found that a small amount of taxifolin was also present along with other components already reported.[1] No glycoside of padmakastein (I) could be obtained and the yields of the components were poor except for sakuranin which was the major product.

EXPERIMENTAL

Extraction of the bark of Prunus puddum.—The sample was collected in the winter of 1956 and supplied by Messrs. Ghose and Co., Darjeeling.

The extraction of the bark (1·2 kg.) was carried out with cold alcohol as given in an earlier paper.[1] The alcoholic extract was distilled under reduced pressure to remove the solvent, water (1 litre) added, the mixture shaken up with ether (800 c.c.) and left in the refrigerator for a month. The crystallised deposit was separated, the ether layer removed and the aqueous solution shaken up and allowed to stand with more ether for another week. More of the colourless solid was obtained. The total yield was 22 g. and it was found to be almost pure sakuranin.

The ether solution was fractionally extracted by means of aqueous sodium carbonate (20%) and aqueous sodium hydroxide (20%). The final ether solution contained very little material. The carbonate solution when acidified and extracted repeatedly with ether, gave a small amount (0·1 g.) of a colourless substance which was fairly soluble in hot water. It gave a brown colour with alcoholic ferric chloride and a bright pink colour with magnesium and hydrochloric acid or with zinc and hydrochloric acid. It

crystallised from dilute methyl alcohol yielding colourless prisms, m.p. 232–34°. It was identified as taxifolin and the mixed m.p. with an authentic sample was undepressed. The sodium hydroxide extract yielded a mixture which was separated into genkwanin (0·2 g.), prunetin (0·2 g.) and sakuranetin (0·5 g.) by the method already described.[1]

When the aqueous solution was subjected to continuous extraction using ethyl acetate, the extracted solid (1 g.) was found to be largely soluble in ether. This ether-soluble portion was repeatedly crystallised from ethyl alcohol when it gave colourless plates, m.p. 230–32°. Further purification was effected by sublimation in vacuum and a final crystallisation from alcohol yielded colourless rectangular plates and prisms, m.p. 238–40°. It gave no colour with magnesium and hydrochloric acid, gave a reddish violet ferric reaction, was insoluble in aqueous sodium carbonate and soluble in aqueous sodium hydroxide to give a yellow solution (Found: C, 66·6; H, 5·1; $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%). It agreed closely in its properties with padmakastein. The identity was further confirmed by preparing its diacetate which crystallised from ethyl acetate as colourless rhombic prisms, m.p. 220–22° (Found: C, 64·6; H, 4·7; $C_{20}H_{18}O_7$ requires C, 64·9; H, 4·9%). Its glycoside could not be detected in this sample of the bark.

Padmakastein dimethyl ether (*II*).—This was prepared by the dimethyl sulphate (excess), potassium carbonate method. The product crystallised from alcohol as colourless thin laminæ, m.p. 152–54° (Narasimhachari and Seshadri,[1] 146–47°). It was insoluble in aqueous alkali, gave no colour with ferric chloride but developed a green colour with concentrated nitric acid (Found: C, 68·3; H, 5·7; $C_{18}H_{18}O_5$ requires C, 68·3; H, 5·7%). It formed a dinitrophenylhydrazone which crystallised from glacial acetic acid as red flakes, m.p. 227°.

Prunetin dimethyl ether (0·5 g.), methyl alcohol (200 c.c.), palladised charcoal (0·15 g., 10%) and a drop of concentrated hydrochloric acid were used for the hydrogenation which was carried out in Paar's low pressure hydrogenation apparatus at 36 lb. per square inch. The hydrogen absorption was over in less than an hour. The product crystallised from alcohol as colourless plates, m.p. 152–54° (Bradbury and White,[3] 156°; Gilbert *et al.*,[7] 154–55°). Mixed m.p. with padmakastein dimethyl ether was undepressed and with prunetin dimethyl ether was considerably depressed. The reduction product gave a green colour with nitric acid identical with that of padmakastein dimethyl ether and a DNP, m.p. 227°, undepressed by the

DNP prepared from the natural sample. The ether underwent smooth oxidation with selenium dioxide to yield prunetin dimethyl ether.

The natural and synthetic samples were also compared using infra-red spectra. Both gave identical spectra. For comparison prunetin dimethyl ether also was studied; its infra-red spectrum differed markedly. Padmakastein dimethyl ether gives a strong peak at 5·95 μ, which corresponds to a carbonyl group of the acetophenone type and this is absent in prunetin dimethyl ether; the peaks at 6·08 μ (shoulder) and 6·10 μ (shoulder) in prunetin dimethyl ether represent the frequency of the carbonyl in conjugation with double bonds on either side.

Padmakastein diacetate (*IV*).—Prunetin diacetate (0·6 g.) dissolved in glacial acetic acid (250 c.c.) was hydrogenated at a pressure of 49 lb. per square inch using palladised charcoal (0·2 g.; 10%). Hydrogenation was complete in eight hours. The catalyst was filtered and the filtrate after removal of acetic acid under reduced pressure gave a product that crystallised from ethyl acetate as glistening colourless rhombic prisms (0·38 g.), m.p. 220–22°, depressed by prunetin diacetate and undepressed by natural padmakastein diacetate (Found: C, 64·6; H, 4·7; $C_{20}H_{18}O_7$ requires C, 64·9; H, 4·9%). The substance underwent oxidation with selenium dioxide in acetic anhydride solution to yield prunetin diacetate.[1]

Padmakastein (*I*).—The synthetic diacetate was boiled under reflux with alcoholic hydrochloric acid for half an hour and the product that separated on cooling and dilution with water, was crystallised from alcohol, m.p. 234–36°. After sublimation in vacuum it was crystallised twice from alcohol when it yielded colourless rectangular plates and prisms, m.p. 238–40°, undepressed by natural padmakastein and considerably depressed by prunetin. It gave an intense green colour with concentrated nitric acid (Found: C, 66·9; H, 4·8; $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%). Yield 0·12 g.

The natural and synthetic samples of padmakastein were also compared using infra-red spectra. Both gave identical spectra. For comparison the infra-red spectrum of prunetin was also taken and it differed markedly. The isoflavanone has the carbonyl frequency at 5·98 μ and the isoflavone at 6·06 μ agreeing with the explanation given already in the case of the methyl ethers.

SUMMARY

The synthesis of padmakastein has been effected by the catalytic reduction of prunetin diacetate and subsequent deacetylation. Similarly

prunetin dimethyl ether yields padmakastein dimethyl ether. The natural and synthetic samples have been compared.

Acknowledgement

We record our thanks to the Council of Scientific and Industrial Research for financial assistance and to Messrs. Sadtler & Co., for infra-red spectra.

References

1. Narasimhachari and Seshadri .. *Proc. Ind. Acad. Sci.*, 1952, **35 A**, 202.
2. Robertson, Suckling and Whalley *J. C. S.*, 1949, 1571.
3. Bradbury and White .. *Ibid.*, 1953, 871.
4. King, King and Warwick .. *Ibid.*, 1952, 96.
5. King and Neill .. *Ibid.*, 1952, 4752.
6. Neill .. *Ibid.*, 1953, 3454.
7. Gilbert, McGookin and Robertson *Ibid.*, 1957, 3740.

NUCLEAR METHYLATION OF CHALKONES AND FLAVANONES

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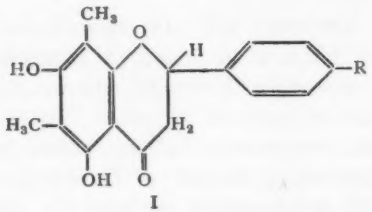
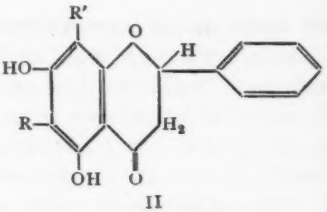
Received July 3, 1958

A number of flavanones with C-methyl groups are known to occur in Nature. They are matteucinol (I *a*), desmethoxy matteucinol (I *b*), farrerol (I *c*), stropopinin (II *a*) and cryptostrobin (II *b*). They have previously been synthesised by starting with nuclear methylated phloroglucinol.[1,2] They should also be capable of synthesis by direct nuclear methylation. With this object in view, a preliminary study (of simpler types) has now been made. When there is no hydroxyl in the 5-position of flavanones, the corresponding chalkones are more stable and could therefore be used for experiments on nuclear methylation. On the other hand when a 5-hydroxyl is present free, the flavanones themselves are quite stable and have to be subjected to nuclear methylation. Typical examples of these two types have now been examined under different conditions.



I

a, R = OCH_3; *b*, R = H; *c*, R = OH

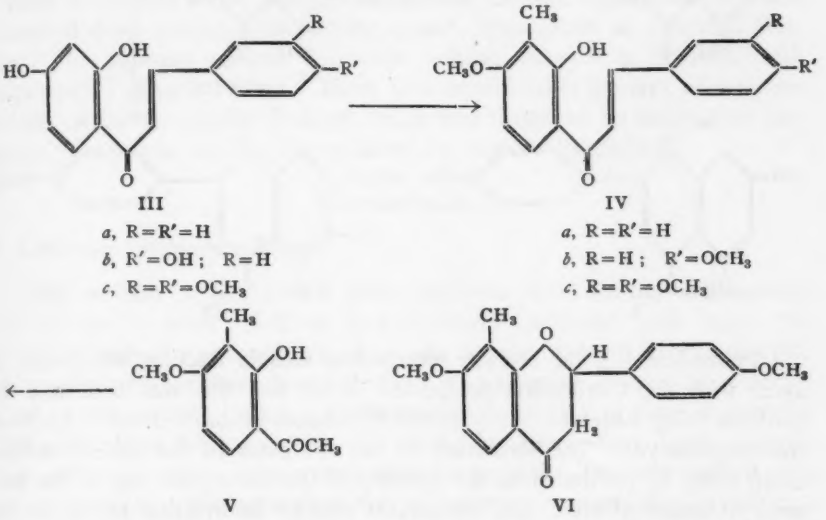


II

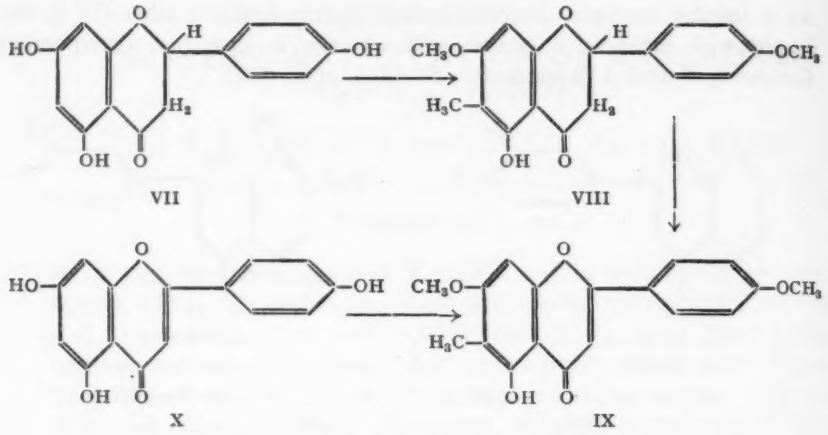
a, R = CH_3; R′ = H
b, R = H; R′ = CH_3

It has been earlier established that carbonyl derivatives of resorcinol, phloroglucinol and 5:7-dihydroxy flavonoids undergo ready C-methylation in the three and six positions respectively when treated with methyl iodide and methanolic alkali.[3] When the 2:4-dihydroxy-chalkones (III) are subjected to nuclear methylation, in all cases C-methylation takes place in the 3-position just as with the corresponding acetophenones. The exact constitution of the methylation products was established by comparing them with the synthetic samples (IV) obtained by the condensation of 2-hydroxy-3-methyl-4-methoxy acetophenone (V) with benzaldehyde, anisaldehyde and veratraldehyde respectively in the presence of alcoholic potash.

As a suitable example, 3-methyl-isoliquiritigenin-dimethyl ether (IV *b*) was heated with alcoholic sulphuric acid whereby it gave the corresponding flavanone, 8-methyl liquiritigenin-dimethyl ether (VI).

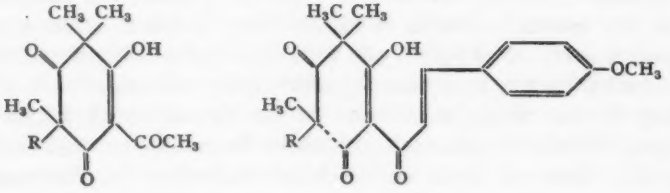


Among flavanones, naringenin (VII) which is readily available has been used for two methods of nuclear methylation: (i) adding excess of methyl iodide first and then methanolic potash slowly during a period of three hours so as to avoid flavanone ring opening as far as possible: (ii) adding excess of methyl iodide and excess of methanolic alkali in one lot and then refluxing for three hours; this should lead to considerable ring opening. In both cases the product was taken up in ether and fractionated using extraction with aqueous sodium bicarbonate, sodium carbonate, aqueous sodium hydroxide, the remaining ether solution retaining the neutral fraction. In method (i) very little was obtained in earlier fractions and the major product was neutral. Though it gave ferric chloride colour, it was very sparingly soluble in alkali. The analytical values agreed with the requirements of 5-hydroxy-7: 4′-dimethoxy-6-methyl flavanone (VIII). This constitution was confirmed by selenium dioxide oxidation to the corresponding flavone which was found to be identical with 5-hydroxy-7: 4′-dimethoxy-6-methyl-flavone (IX) obtained by nuclear methylation of apigenin (X). Hence it could be concluded that when the flavanone ring is kept intact it undergoes nuclear methylation in the 6-position just as flavones and flavonols.



In method (ii), the sodium bicarbonate soluble fraction was found to agree with the C-trimethyl compound (XI *a*) and this was confirmed by synthesis using 5-acetyl-1 :3 :3-trimethyl-cyclohexen-(4)-*ol*-(4)-dione-(2 :6) (XI *a*) and anisaldehyde. The formation of the substance in the nuclear methylation could be attributed to the opening of the hetrocyclic ring in the presence of excess of alkali and subsequent nuclear methylation just as in the case of carbonyl derivatives of phloroglucinol.[4] The sodium carbonate fraction was found to be the C-tetramethyl compound (XII *b*) both from a study of its properties and also by its synthesis employing 5-acetyl-1 : 1 : 3 : 3-tetramethyl-cyclohexen-(4)-*ol*-(4)-dione-(2 : 6) (XI *b*) and anisaldehyde.

The sodium hydroxide fraction was a yellow crystalline solid, m.p. 156–57°, obtained in very poor yield. With alcoholic ferric chloride it gave brown colour. Because of small yield it was not further studied. The neutral fraction was found to be minor in quantity and was identified as 5-hydroxy-7 : 4′-dimethoxy-6-methyl flavanone (VIII) obtained conveniently by method (i).



XI XII

a, R=H ; *b*, R=CH_3

In connection with the identification of the nuclear methylated flavanone, the nuclear methylation of apigenin (X) has now been carried out using sodium methoxide and excess of methyl iodide. As in other cases it yields about 10% of the 6-methyl compound (IX) the constitution of which is derived from analogy with similar cases.[5] This comes as a neutral fraction. The aqueous sodium hydroxide soluble fraction is identical with apigenin-7:4′-dimethyl ether. There is a considerable amount of aqueous sodium carbonate soluble fraction which was found to be unchanged apigenin. There was no fraction extracted by sodium bicarbonate.

EXPERIMENTAL

2:4-*Dihydroxychalkone* (*III a*)

The method of preparation using alcoholic alkali for the condensation did not give a good yield of 2:4-dihydroxy chalkone[6] and hence the following method was employed: A steady current of dry hydrogen chloride gas was passed for three hours through an ice-cooled solution of resacetophenone dibenzoate (14 g.) and benzaldehyde (5 c.c.) in dry ethylacetate (200 c.c.). After leaving in the ice chest for twenty-four hours, ligroin was added in excess, when a dark red oil separated. This was washed with water, dissolved in alcohol and refluxed with aqueous potash (20 g. in 300 c.c.) for three hours. The product was cooled, acidified to Congo red and most of the alcohol removed by distillation under reduced pressure. The solid that separated was filtered, washed with boiling water, dried and crystallised twice from benzene yielding yellow needles (4 g.), m.p. 147–48° alone or when mixed with an authentic sample of 2:4-dihydroxy chalkone. It gave a dark reddish brown colour with alcoholic ferric chloride.

2-*Hydroxy*-3-*methyl*-4-*methoxychalkone* (*IV a*)

(i) *By chalkone condensation.*—Aqueous potassium hydroxide (3 g. in 3 c.c.) was added little by little to a solution of 2-hydroxy-3-methyl-4-methoxy-acetophenone[7] (1·8 g.) and benzaldehyde (1·1 c.c.) in alcohol (30 c.c.). The resulting solution after keeping tightly corked for twenty-four hours at room temperature, was diluted with water, cooled and acidified with dilute hydrochloric acid. The pale yellow precipitate was filtered, washed with sodium bicarbonate solution and crystallised from methyl alcohol when deep yellow rectangular rods and prisms (1·2 g.) were formed; m.p. 132–33° (Found: C, 75·3; H, 6·3; $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%). It was sparingly soluble in aqueous sodium hydroxide and yielded a reddish brown colour with alcoholic ferric chloride.

(ii) *By nuclear methylation of* 2: 4-*dihydroxychalkone* (*III a*).—A solution of chalkone (2 g.) in methanolic potash (2·5 g. in 25 c.c.) was cooled in ice, treated with methyl iodide (5 c.c.) and left in a well stoppered flask in an ice bath which was allowed to assume the laboratory temperature slowly. After keeping overnight, the resulting mixture was boiled under reflux for six hours with more of methyl iodide (2 c.c.). The alcohol was distilled off under vacuum, and the residue acidified and extracted with ether. The ether concentrate was dissolved in the minimum amount of methyl alcohol and the solution cooled. The sparingly soluble fraction was crystallised thrice from methanol when it formed deep yellow rectangular rods and prisms (0·5 g.) melting at 132–33° alone or when mixed with 2-hydroxy-3-methyl-4-methoxychalkone reported above.

The methanolic mother liquor yielded a product (1·2 g.) which crystallised from ethyl acetate-petroleum ether mixture as pale yellow needles melting at 105° alone or when mixed with an authentic sample of 2-hydroxy-4-methoxychalkone.[8]

2-*Hydroxy*-3-*methyl*-4: 4′-*dimethoxychalkone* (*IV b*)

(i) *By chalkone condensation.*—2-Hydroxy-3-methyl-4-methoxyaceto-phenone (1·8 g.) and anisaldehyde (1·4 g.) were condensed with alcoholic potash (3 g. in 30 c.c.) in the same way as described earlier. The product crystallised from methyl alcohol as deep yellow rods (1·4 g.) melting at 145–46° (Found: C, 72·4; H, 6·5; $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·1%). It was sparingly soluble in alkali, dissolved in concentrated sulphuric acid to an orange solution and yielded a reddish brown colour with alcoholic ferric chloride.

(ii) *By nuclear methylation.*—Isoliquiritigenin (III *b*) was prepared by a modification of the method of Nadkarni and Wheeler.[6] The crude product was taken up in ether and washed with limited quantities of aqueous sodium bicarbonate in order to remove *p*-hydroxybenzoic acid, washed with water and the ether solution evaporated. The chalkone is best crystallised from a large volume of benzene, m.p. 204–05°.

Isoliquiritigenin (III *b*) (2 g.) was methylated exactly in the same way as mentioned in the case of 2: 4-dihydroxychalkone and the product fractionated using methyl alcohol. The sparingly soluble fraction, after two further crystallisations from methanol, yielded 2-hydroxy-3-methyl-4: 4′-dimethoxychalkone as deep yellow rectangular rods and prisms (0·5 g.) m.p. 145–46° alone or when mixed with the sample obtained by synthesis. The methanolic mother liquor yielded 2-hydroxy-4: 4′-dimethoxychalkone (1·3 g.) as yellow needles,[9] m.p. 113–14°.

3-Methyl-2: 4: 4′-trimethoxychalkone:

The samples of the above chalkone (0·5 g.) prepared by the two methods were separately heated with dimethyl sulphate (0·5 c.c.) and ignited potassium carbonate (2 g.) in acetone solution for 30 hours. The product was found to be the same, 3-methyl-2: 4: 4′-trimethoxy-chalkone crystallising from ethylacetate-petroleum ether mixture as colourless stout rectangular prisms, m.p. 103–04°. It gave no ferric reaction and formed an orange solution with concentrated sulphuric acid (Found: C, 73·2; H, 6·5; $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·5%).

7: 4′-Dimethoxy-8-methyl-flavanone [*8-Methyliquiritigenin dimethyl ether* (*VI*)]

2-Hydroxy-4: 4′-dimethoxy-3-methylchalkone (IV *b*) (0·1 g.) was refluxed with 4% alcoholic sulphuric acid (50 c.c., containing 10 c.c. of water) for 48 hours. Alcohol was removed under reduced pressure and water was added to the residue. The solid that separated was filtered and fractionally crystallised (five times) from alcohol when colourless needles (10 mg.), m.p. 110–11° separated. It gave no colour with alcoholic ferric chloride.

2-Hydroxy-3-methyl-4: 3′: 4′-trimethoxychalkone (*IV c*)

(i) *By chalkone condensation.*—2-Hydroxy-3-methyl-4-methoxy-acetophenone (1·8 g.) and veratraldehyde (1·6 g.) were condensed with alcoholic potash and the product crystallised from methyl alcohol yielding deep yellow long prismatic rods, m.p. 163–64°. It was sparingly soluble in alkali, dissolved in concentrated sulphuric acid to an orange red solution and gave a brown colour with alcoholic ferric chloride (Found: C, 69·6; H, 6·3; $C_{19}H_{20}O_5$ requires C, 69·5; H, 6·1%).

(ii) *By nuclear methylation of butein-3′: 4′-dimethyl ether* (*III c*).—Butein-3′: 4′-dimethyl ether (III *c*) was obtained by the method of Mauthner[10] but it was found to melt at 202–03° after crystallisation from benzene. Mauthner reported the m.p. as 127–28°, while Goschke and Tambor[11] reported its m.p. as 203°.

The above chalkone (1·75 g.) was subjected to nuclear methylation as described earlier. The sparingly soluble fraction (0·55 g.) (methanol) had m.p. 163–64° alone or when mixed with 2-hydroxy-3-methyl-4: 3′: 4′-trimethoxy chalkone (IV *c*). The mother liquor yielded butein 4: 3′: 4′-trimethyl ether,[12] m.p. 156–58°.

3-Methyl-butein-tetramethyl ether

This was obtained by methylation of the above chalkone (IV *c*) with dimethyl sulphate and potassium carbonate. It crystallised from ethyl

acetate-petroleum ether mixture as colourless tiny prisms, m.p. 194–95° (Found: C, 70·7; H, 6·5; $C_{20}H_{22}O_5$ requires C, 70·2; H, 6·5%).

Nuclear methylation of naringenin (VII)

Method (I): (*5-hydroxy-6-methyl-7: 4′-dimethoxy flavanone, VIII*).—Naringenin (10 g.) was dissolved in anhydrous methanol (100 c.c.) and the solution refluxed with methyl iodide (30 c.c.) for three hours during which time methanolic potash (10 g./40 c.c.) was added in ten lots and more of methyl iodide (10 c.c.) was added during the reaction to compensate for loss by vapourisation. Excess of methyl iodide and methyl alcohol were distilled off under reduced pressure and water (500 c.c.) added. The solution was acidified with cold concentrated hydrochloric acid and extracted with ether. The ether solution was extracted with saturated aqueous sodium bicarbonate, 5% sodium carbonate and 4% sodium hydroxide. The extracts yielded no appreciable product on acidification. The remaining ether solution was washed with water three times, dried over anhydrous sodium sulphate, ether distilled off and the residue crystallised from methanol, yielding colourless needles, m.p. 148° (1 g.). It gave a bluish violet colour with alcoholic ferric chloride (Found: C, 68·4; H, 6·3; $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·8%).

5-Hydroxy-7: 4′-dimethoxy-6-methyl flavone (IX)

(*a*) *By selenium dioxide oxidation.*—The above C-methyl-flavanone (VIII) (0·1 g.) was dissolved in acetic anhydride (6 c.c.), selenium dioxide (0·2 g.) added and the mixture heated under reflux at 140° for five hours. The mixture was filtered off and acetic anhydride removed under reduced pressure. Water was added to the residue and the solid that separated was filtered, washed with cold water and crystallised from methyl alcohol forming pale straw coloured needles (0·05 g.), m.p. 183–85° undepressed by the nuclear methylation product of apigenin (*see* below). It gave a green colour with alcoholic ferric chloride (Found: C, 68·7; H, 4·7; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%).

(*b*) *By nuclear methylation of apigenin (X)*.—Apigenin (X) (2·7 g.), sodium methoxide from sodium (2·5 g.) and absolute methanol (50 c.c.) were employed following the method used earlier.[5] The method of working was, however, different and was as follows. The ether extract of the product was washed successively with saturated aqueous sodium bicarbonate (no extraction), 5% sodium carbonate (Fraction I) and 4% sodium hydroxide (Fraction II), the remaining ether solution contained neutral Fraction (III). Fraction (I) on acidification yielded a pale yellow compound, m.p. 343°

alone or mixed with apigenin. It gave a dark brown colour with alcoholic ferric chloride. Fraction (II) was acidified and the solid product crystallised from alcohol yielding a yellow compound, m.p. 270–71° undepressed by an authentic sample of apigenin-7: 4′-dimethyl ether. It gave a dark brown colour with alcoholic ferric chloride. Neutral Fraction (III) on concentration gave a solid which crystallised from methanol as straw coloured needles, m.p. 183–85°, alone or admixed with the sample of (IX) obtained by selenium dioxide oxidation.

Method (II) (Polymethylated chalkones).—Naringenin (VII) (10 g.) was dissolved in dry methanol (100 c.c.) and methyl iodide (40 c.c.) and methanolic potash (10 g. in 40 c.c.) added all at once. The mixture was refluxed for three hours, excess of methyl iodide and methanol removed under reduced pressure and the residue treated with cold water (500 c.c.). The solution was acidified with cold concentrated hydrochloric acid and repeatedly extracted with ether. The ether solution was then successively extracted with saturated aqueous sodium bicarbonate (Fraction A), 5% sodium carbonate (Fraction B), 4% sodium hydroxide (Fraction C) and the remaining ether solution was then washed with water and dried over anhydrous sodium sulphate (neutral Fraction D).

Fraction A [5-(4′-*methyoxy-cinnamoyl*)-1: 3: 3-*trimethyl-cyclohexen*-(4)-ol-(4)-*dione*-(2: 6)] (*XII a*):

The solution (200 c.c.) was acidified in the cold with concentrated hydrochloric acid. On keeping in the refrigerator overnight a yellow solid separated, which was filtered and crystallised from methanol yielding golden yellow rectangular tablets (3 g.), m.p. 177–78°, alone or when mixed with the synthetic sample described below. With alcoholic ferric chloride it gave a reddish brown colour and formed an organge yellow solution in concentrated sulphuric acid (Found: C, 69·7; H, 6·5; $C_{19}H_{21}O_5$ requires C, 69·5; H, 6·4%).

Synthesis.—5-Acetyl-1: 3: 3-trimethyl-cyclo-hexen-(4)-*ol*-(4)-dione-(2: 6)[4] (XI *a*) (2·2 g.) and anisaldehyde (1·6 c.c., 1·1 mole) were dissolved in alcohol (200 c.c.) treated with aqueous caustic potash (12 g. in 10 c.c.) and kept at room temperature for forty-eight hours. It was then diluted with an equal volume of water and extracted with ether to remove excess of anisaldehyde. The aqueous solution was acidified under cooling with dilute hydrochloric acid. The mixture was extracted with ether, the extract dried over anhydrous sodium sulphate and evaporated. The residue crystallised from methanol as golden yellow rectangular tablets (0·55 g.), m.p. 177–78° undepressed by the above sample. The colour reactions were the same.

Fraction B [5-(4′-*methoxy-cinnamoyl*)-1 : 1 : 3 : 3-*tetra-methyl-cyclohexen*-(4)-ol-(4)-*dione*-(2 : 6)] (*XII b*):

The sodium carbonate extract was acidified with cold dilute hydrochloric acid and cooled in ice. The deep yellow solid product was filtered and crystallised from methanol to give yellow thin rectangular plates (3 g.), m.p. 108° alone or when mixed with a synthetic sample. It gave reddish brown colour with alcoholic ferric chloride and formed a yellow solution in concentrated sulphuric acid (Found: C, 69·2; H, 6·6; $C_{20}H_{22}O_5$ requires C, 69·7; H, 6·6%).

Synthesis.—5-Acetyl-1 : 1 : 3 : 3-tetramethyl-cyclohexen-(4)-*ol*-(4)-dione-(2 : 6)[4] (XI *b*), anisaldehyde (1·4 c.c., 1·1 mols) were condensed just as in the preparation of (XII *a*). The product crystallised from methanol to give deep yellow thin rectangular plates (0·8 g.), m.p. 108°. It gave a reddish brown colour with alcoholic ferric chloride and a yellow solution in concentrated sulphuric acid.

Neutral Fraction D [5-*Hydroxy*-6-*methyl*-7 : 4′-*dimethoxy flavanone* (*VIII*)]

The ether solution was distilled and the residue (0·2 g.) crystallised from methanol when colourless needles separated, m.p. 148° undepressed by the 5-hydroxy-6-methyl-7 : 4′-dimethoxyflavanone (VIII) sample obtained from the first method.

SUMMARY

Nuclear methylation of 2 : 4-dihydroxy-chalkones (III) give rise to 3-C-methyl derivatives just as in the case of resacetophenone. C-Methyl-chalkone-derivatives (IV) with substituents in the side phenyl nucleus have also been prepared by this method. For comparison, they have been synthesised using 3-methyl-peonol and appropriate derivatives of benzaldehyde. C-Methyl-*iso*-liquiritigenin-dimethyl-ether (IV *b*) was cyclised to the corresponding 8-methyl-flavanone (VI).

The flavanone, naringenin, when subjected to nuclear methylation under mild conditions yields 6-methyl-flavanone derivative (VIII) whereas under conditions in which the oxygen ring opens, beside the above 6-methyl flavanone (VIII), poly-C-methylated chalkones (XII *a* + *b*) are formed just as in case of phloracetophenone.

REFERENCES

1. Fujise and Nishi .. *Ber.*, 1933, **66**: 929; *J. Pharm. Soc., Japan*, 1934, **55**, 1020.

——— and Kubota .. *Ber.*, 1934, **67**, 1905.

2. Lindstedt and Misiorny .. *Acta. Chem. Scand.*, 1951, **5**, 1.
3. Jain and Seshadri .. *Quart. Rev.*, 1956, **10**, 169–84.
4. ———— .. *Proc. Ind. Acad. Sci.*, 1955, **42 A**, 279.
5. Mukerjee and Seshadri .. *Ibid.*, 1953, **38 A**, 207.
6. Wheeler .. *J.C.S.*, 1938, 1320.
7. Rangaswami and Seshadri .. *Proc. Ind. Acad. Sci.*, 1938, **8 A**, 215.
8. Emalevicz and Kostanecki .. *Ber.*, 1899, **32**, 311.
9. Kostanecki and Osius .. *Ibid.*, 1899, **32**, 322.
10. Mauthner .. *Math. naturw. Anz. Ungar. Akad. Wiss.*, 1943, **62**, 355.
11. Goschke and Tambor .. *Ber.*, 1912, **45**, 185.
12. Bargellini and Finkelstein .. *Gazetta*, **42** (2), 425.

SOLUTION OF CAUCHY'S PROBLEM FOR THE WAVE EQUATION

$$\left(\frac{\partial^2}{\partial t^2} - \nabla^2 + k^2\right)\psi = 0$$

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1. INTRODUCTION

COPSON (1956) has given a method for the solution of the Cauchy's problem for the wave equation

$$\frac{\partial^2 u}{\partial t^2} - \nabla^2 u = 0 \tag{1}$$

in space of any odd number of spatial dimensions. In the usual method, one gets an infinite integral over the characteristic cone. Copson was able to avoid this difficulty of the divergent integral by generalising the theory of the wave equation in one spatial dimension to an odd number of spatial dimensions. In view of the physical importance of the damped wave equation

$$\frac{\partial^2 u}{\partial t^2} - \nabla^2 u + k^2 u = 0 \tag{2}$$

we think it is of interest to extend Copson's method to the solution of the equation (2). We make this extension below.

2. NOTATION

We take a system of rectangular Cartesian co-ordinates $x_1, x_2, \ldots, x_{2m-1}$ in a space of $2m - 1$ dimensions and write

$$\mathrm{L} \equiv \frac{\partial^2}{\partial t^2} - \nabla_x{}^2 + k^2, \tag{3}$$

$$\nabla_x{}^2 = \sum_{i=1}^{2m-1} \frac{\partial^2}{\partial x_i{}^2}. \tag{4}$$

The corresponding operators in ξ-τ space will be denoted by Λ and ∇_ξ^2:—

$$\Lambda = \frac{\partial^2}{\partial \tau^2} - \nabla_\xi^2 + k^2 \tag{5}$$

$$\nabla_\xi^2 = \sum_{i=1}^{2m-1} \frac{\partial^2}{\partial \xi_i^2}. \tag{6}$$

We also write

$$r^2 = (x - \xi)^2 = \sum_{i=1}^{2m-1} (x_i - \xi_i)^2 \tag{7}$$

and

$$s = [(t - \tau)^2 - r^2]^{\frac{1}{2}}. \tag{8}$$

3. A Lemma on the Wave Operator

We shall prove the following:

Lemma:—If u along with its partial derivatives upto order $(m-1)$ is continuous and if

$$\mathrm{U}(x, t) = \int_{\mathrm{D}} \mathrm{J}_0(ks)\, u(\xi, \tau)\, d\xi\, d\tau, \tag{9}$$

then

$$\mathrm{L}^m \mathrm{U}(x, t) = 2^{2m-1} \pi^{m-1} \Gamma(m)\, u(x, t). \tag{10}$$

Here $\mathrm{J}_0(ks)$ represents the Bessel function of order zero. Denoting the instant at which the Cauchy data is given by t_0, the region, D, of integration in (9) is defined by

$$s^2 \geqslant 0; \quad \tau - t < 0, \quad \tau \geqslant t_0$$

and is bounded by a part V′ of the retrograde characteristic cone and by a part V of the hyperplane $\tau = t_0$ (Fig. 1).

To prove the lemma, let us define a function

$$\mathrm{W}^{(2\alpha)}(x, t;\ \xi, \tau) = \frac{1}{2^{\alpha+m-1} \pi^{m-1} \Gamma(\alpha)} (ks)^{\alpha-m} \mathrm{J}_{\alpha-m}(ks) \tag{11}$$

where α is a complex parameter and $\mathrm{J}_{\alpha-m}(ks)$ is Bessel function of order $\alpha - m$. A straightforward differentiation of (11) shows that, if α is sufficiently large,

$$\mathrm{L}\mathrm{W}^{(2\alpha+2)}(x, t;\ \xi, \tau) = k^2\, \mathrm{W}^{(2\alpha)}(x, t;\ \xi, \tau). \tag{12}$$

We now define an integral of fractional order 2α by

$$I^{(2\alpha)} u(x, t) = k^{2m} \int_D W^{(2\alpha)}(x, t;\ \xi, \tau)\, u(\xi, \tau)\, d\xi\, d\tau. \tag{13}$$

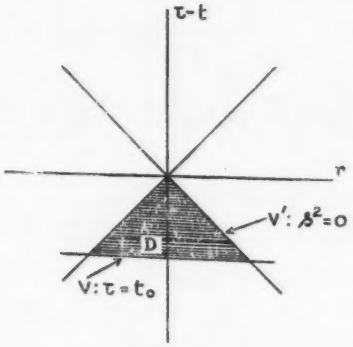

FIG. 1

If we write the Bessel function as a series in powers of its argument and test the convergence of each integral separately (Riesz 1949), we can easily see that (13) converges if Rl. $\alpha > m - 1$. Moreover, all the terms in this expansion, excepting the first term, involve α as a factor and therefore become zero if $\alpha \to 0$. Considered as a function of α, the first term can be analytically continued into Rl. $\alpha > 0$, and its limit as $\alpha \to +0$ is $u(x, t)$ (Fremberg, 1945; Copson, 1947; Majumdar and Gupta, 1948, 1949). Therefore, the analytic continuation of (13) to $\alpha = +0$ exists and

$$\underset{\alpha \to +0}{\text{Lt.}}\ I^{(2\alpha)} u(x, t) = u(x, t). \tag{14}$$

When α is sufficiently large, we get, on using (12) in (13),

$$LI^{(2\alpha+2)} u(x, t) = k^2 I^{2\alpha} u(x, t) \tag{15}$$

and, hence,

$$L^m I^{(2\alpha+2m)} u(x, t) = k^{2m} I^{(2\alpha)} u(x, t). \tag{16}$$

Letting $\alpha \to +0$, we find on using (14)

$$L^m I^{(2m)} u(x, t) = k^{2m} u(x, t). \tag{17}$$

Now

$$I^{(2m)} u(x, t) = k^{(2m)} \int_D W^{2m}(x, t;\ \xi, \tau)\, u(\xi, \tau)\, d\xi\, d\tau$$

$$= \frac{k^{2m}}{2^{2m-1}\pi^{m-1}\Gamma(m)} \int_D J_0(ks)\, u(\xi, \tau)\, d\xi\, d\tau$$

so that (17) gives

$$\frac{1}{2^{2m-1}\pi^{m-1}\Gamma(m)} \mathrm{L}^m \int_{\mathrm{D}} \mathrm{J}_0(ks)\, u(\xi, \tau)\, d\xi\, d\tau = u(x, t)$$

which is our lemma, equations (9) and (10).

4. Solution of the Wave Equation (2)

To solve the wave equation (2) with the initial conditions

$$u(x, t)\Big|_{t=t_0} = f(x), \quad \frac{\partial u}{\partial t}\Big|_{t=t_0} = g(x), \tag{18}$$

we consider the integral

$$\mathrm{G} \equiv \int_{\mathrm{D}} (u \Lambda v - v \Lambda u)\, d\xi\, d\tau \tag{19}$$

with

$$v = (ks)\, \mathrm{J}_1(ks). \tag{20}$$

Putting $\alpha = m$ in (12) and noting that

$$v = 2^{2m} \pi^{m-1}\, \Gamma(m+1)\, \mathrm{W}^{(2m+2)}, \tag{21}$$

we get

$$\Lambda v = 2mk^2 \mathrm{J}_0(ks) \tag{22}$$

Using (22) and (2) in (19),

$$\begin{aligned} \mathrm{G} &= \int_{\mathrm{D}} u \Lambda v\, d\xi\, d\tau \\ &= 2mk^2 \int_{\mathrm{D}} \mathrm{J}_0(ks)\, u(\xi, \tau)\, d\xi\, d\tau \\ &= 2mk^2\, \mathrm{U}(x, t) \\ &\qquad\qquad \text{[from (9)]} \end{aligned} \tag{23}$$

On the other hand, we can transform the integral (19) into a surface integral by using Green's theorem. If $(\omega, \lambda_1, \lambda_2, \ldots, \lambda_{2m-1})$ denote the direction cosines of the outward drawn normal to the boundary, S, of D, we get

$$\mathrm{G} = \int_{\mathrm{S}} \left[\left(u \frac{\partial v}{\partial \tau} - v \frac{\partial u}{\partial \tau} \right) \omega - \sum_{i}^{2m-1} \left(u \frac{\partial v}{\partial \xi_i} - v \frac{\partial u}{\partial \xi_i} \right) \lambda_i \right] d\mathrm{V}. \tag{24}$$

The surface, S, is made up of two parts, V and V′ (*see* Fig. 1). On V,

$$\tau = t_0, \qquad r^2 \leqslant (t - t_0)^2$$

$$\omega = 1, \qquad \lambda_1 = \lambda_2 = \ldots\ldots = \lambda_{2m-1} = 0.$$

Hence, the integral over V is

$$G_V = \int_V \left[u \frac{\partial v}{\partial \tau} - v \frac{\partial u}{\partial \tau} \right] dV$$

$$= \int_V \left[f(\xi) \frac{\partial v}{\partial \tau} - g(\xi)\, v \right] dV$$

[using (18)]

$$= \int_V \left[f(\xi) \cdot \frac{-\partial v}{\partial t} - g(\xi)\, v \right] dV$$

$$= -\frac{\partial}{\partial t} \int_V f(\xi)\, v dV - \int_V g(\xi)\, v dV$$

On the surface V′ (Fig. 1), $s^2 = 0$, so that $v = 0$. Therefore, from (24), the integral over V′ becomes

$$G_{V'} = \int_V \left[u \frac{\partial v}{\partial \tau} \omega - \sum_1^{2m-1} u \frac{\partial v}{\partial \xi_i} \lambda_i \right] dV \tag{26}$$

We have

$$\omega = \frac{1}{\sqrt{2}}, \quad \lambda_i = \frac{\xi_i - x_i}{\sqrt{2}\,(t - \tau)} \tag{27}$$

Now

$$\frac{\partial v}{\partial \tau} = \frac{\partial (ks)}{\partial \tau} \frac{\partial}{\partial (ks)} [(ks)\, J_1(ks)]$$

$$= k \frac{\partial s}{\partial \tau} (ks)\, J_0(ks) \tag{28 a}$$

and

$$\lambda_i \frac{\partial v}{\partial \xi_i} = \lambda_i \frac{\partial (ks)}{\partial \xi_i} \frac{\partial}{\partial (ks)} [(ks)\, J_1(ks)]$$

$$= k\lambda_i \frac{\partial s}{\partial \xi_i} (ks)\, J_0(ks) \tag{28 b}$$

Both (28 *a*) and (28 *b*) are proportional to s and therefore vanish on the surface V'. It follows that

$$G_{V'} = 0 \tag{29}$$

so that (24) becomes [*see* (25) and (29)]

$$G = G_V + G_{V'} = G_V$$

$$= \frac{-\partial}{\partial t} \int_V f(\xi)\, v dV - \int_V g(\xi)\, v dV \tag{30}$$

From (23) and (30), we get

$$2mk^2\, U(x, t) = \frac{-\partial}{\partial t} \int_V f(\xi)\, v dV - \int_V g(\xi)\, v dV \tag{31}$$

Operating on both sides by L^m and using (10), we now obtain

$$2^{2m} \pi^{m-1}\, \Gamma(m+1)\, k^2\, u(x, t)$$

$$= - L^m \left[\frac{\partial}{\partial t} \int_V f(\xi)\, v dV + \int_V g(\xi)\, v dV \right]$$

Hence, the solution of the wave equation (2) with the initial conditions (18) is

$$u(x, t) = - \frac{1}{2^{2m} \pi^{m-1}\, \Gamma(m+1)\, k^2} \cdot L^m \left[\frac{\partial}{\partial t} \int_V f(\xi)\, v dV \right.$$

$$\left. + \int_V g(\xi)\, v dV \right] \tag{32}$$

where L is the operator defined in (3), the function v is defined by (20) and V is the hyperplane $\tau = t_0$ bounding the retrograde characteristic cone (Fig. 1).

SUMMARY

A method given by Copson has been generalised here to obtain a solution of Cauchy's problem for the wave equation $\partial^2 u/\partial t^2 - \nabla^2 u + k^2 u = 0$ in any odd number of spatial dimensions. The method does not involve the use of any device for evaluating the divergent integrals.

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REFERENCES

1. Copson, E. T. .. *Proc. Edin. Math. Soc.*, 1947, **8** (2), 25–36.
2. ———— .. *Proc. Roy. Soc.*, 1956, **235 A**, 560–72.
3. Fremberg, N. E. .. *K. fysiogr. Sallsk, Lund Forh.*, 1945, **15**, 27.
4. Majumdar, R. C. and Gupta, S. *Nature*, 1948, **161**, 410 and *Phys. Rev.*, 1949, **75**, 12.
5. Riesz, M. .. *Acta Math.*, 1949, **81**, 1–223.

THE SPECTRUM OF IODINE EXCITED IN THE PRESENCE OF ARGON

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Abstract

The band systems of iodine in the regions 3455–3015 Å, 2785–2750 Å and 2730–2520 Å obtained by earlier workers using prism spectrographs are now photographed in the first and second orders of a 21-ft. grating spectrograph. A large number of new bands are obtained in all these three systems which are now extended to the regions 3461–3015 Å, 2785–2731 Å and 2729–2486 Å. The wavelengths and wavenumbers of all the bands are recorded along with their visually estimated intensities. The Deslandres schemes for the three systems representing all the bands are given and are found to be supported by the corresponding intensity distributions of the expected type. It was found that the two systems 3460–3015 Å and 2785–2731 Å do not involve for their lower levels the ground state as assumed by the earlier workers but the $^3\Pi_u$ (O_u^+) state at 15642 cm.$^{-1}$, which is also the lower state for the 4420–4000 Å system. The band system in the region 2730–2486 Å has for its lower level the ground state of the molecule as reported by the earlier workers. A reanalysis of this system made to include all the bands observed in the present experiments, gave vibrational constants slightly different from those obtained by earlier workers. The vibrational constants of the upper states of the four different systems that one gets by exciting iodine in the presence of argon are

System	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$
4400–4000 Å ..	41411 cm.$^{-1}$	102·2 cm.$^{-1}$	0·34 cm.$^{-1}$	..
3460–3015 Å ..	45937 „	103·7 „	0·095 „	..
2785–2731 Å ..	51847 „	112·4 „	0·711 „	0·004 cm.$^{-1}$
2730–2486 Å ..	47207 „	96·5 „	0·510 „	0·0033 „

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It was found that the 3460–3015 Å, 2785–2731 Å and 4420–4000 Å systems of iodine are respectively analogous to the 2950–2670 Å, 2660–2590 Å and 3150–2970 Å systems of bromine.

INTRODUCTION

THE spectrum of iodine obtained by electrical[1–4] or fluorescent[5–8] excitation shows discrete band system in the region 6700–5000 Å and groups of diffuse bands in the region 4800–2500 Å. The discrete band system in emission is known to be identical with that in absorption. The groups of diffuse bands were explained earlier by Venkateswarlu[1–3] as due to transitions from upper stable electronic states to lower repulsive states dissociating into $^2P + {}^2P$ normal iodine atoms.

By fluorescent excitation of a mixture of iodine and nitrogen Elliott[9] reported four band systems in the regions 4630–4440 Å, 4321–4041 Å, 3450–3040 Å and 2730–2520 Å. Waser and Wieland[10] excited a mixture of iodine vapour and argon by high frequency discharge and obtained only the last three of the band systems obtained by Elliott. They attributed the 4630–4440 Å system to IN molecule. Venkateswarlu[11] later excited the iodine vapour in the presence of argon by a transformer discharge and obtained the above band systems together with a weak system in the region 2785–2750 Å. Since he used a transformer discharge he obtained larger number of bands in these systems than the earlier workers. Venkateswarlu using Rank's constants[12] for the ground state of iodine molecule, then available, analysed all the bands in the region 3455–3015 Å as due to a transition from a level at $T_e = 39186{\cdot}8$ cm.$^{-1}$ with $\omega_e' = 103{\cdot}1$ cm.$^{-1}$ to the ground state of the molecule. Rank and Baldwin[13] later published the revised vibrational constants for the ground state of the iodine molecule. Wieland and Waser[14] using these revised constants with a change in the $\omega_e t_e$ term represented the bands in the region 3455–3237 Å as belonging to a transition from an upper level at $T_e = 33346{\cdot}6$ cm.$^{-1}$ with $\omega_e' = 104{\cdot}0$ cm.$^{-1}$ and $\omega_e' x_e' = 0{\cdot}2$ cm.$^{-1}$ to the ground state of the molecule. Using the experimental data of earlier workers and adding an additional higher order positive term to the Rank and Baldwin's constants, Mathieson and Rees[15] analysed the bands in the region 3455–3015 Å as due to a transition from a state at $T_e = 39293$ cm.$^{-1}$ with $\omega_e' = 110{\cdot}9$ cm.$^{-1}$ to the ground state of the molecule. But none of the abovementioned workers showed from the analysis any corresponding intensity distribution or Frank-Condon parabola for the band system. The 3455–3015 Å system of iodine which is the most intense of all the systems obtained by exciting iodine in the presence of argon appears to

be analogous† to the recently obtained 2950–2670 Å system of bromine discussed by Venkateswarlu and Verma,[16] which is again the most intense system of all the systems of bromine obtained under similar conditions. The vibrational analysis supported by the corresponding intensity distribution and the probable observed isotopic shifts as discussed by Venkateswarlu and Verma showed that the lower state of the system 2950–2670 Å of bromine is the $^3\Pi_u$ (O_u^+) state and not the ground state of the molecule. This observation suggests that the lower state of the system 3455–3015 Å of iodine, may also be $^3\Pi_u$ (O_u^+) and not the ground state. It was felt that to settle this point it would be necessary to have better experimental data than those available from the earlier workers. Therefore this band system of iodine is photographed on the first and second orders of a 21-ft. grating spectrograph and the results obtained along with the corresponding vibrational analysis are given and discussed in this paper.

It was also felt that the analysis and interpretations of the band systems 2785–2750 Å and 2730–2520 Å could also be improved if they are worked out with a spectrograph of higher resolution and dispersion than those used by earlier workers. Accordingly these systems are also photographed with a first order 21-ft. grating spectrograph and the results obtained are included in this paper along with the corresponding analyses and discussion.

The Band System in the Region 3460–3015 Å

The band system was photographed in the region 3460–3145 Å with a 21-ft. grating spectrograph using the apparatus and experimental conditions similar to those described by Venkateswarlu and Verma[16] for bromine. Figure 1 shows the photograph of the spectrum obtained and Table I the wavelengths and wave numbers of the band heads along with their visually estimated intensities. The wavenumbers obtained from measurements of different plates did not differ from one another by more than ± 1 cm.$^{-1}$ But, as there is certain overlapping of the neighbouring bands, it is expected that the error involved in the determination of the actual position of the band heads may be ± 2 or ± 3 cm.$^{-1}$ The wavelengths of the band heads as reported earlier by Venkateswarlu[11] are also included in the table for comparison along with those obtained by Elliott[9] in fluorescence. It can be seen from the table that a large number of new bands are obtained in the present experiments.

† It may be mentioned that it is exactly in the same regions of these two systems that one obtains the most intense parts of the groups of diffuse bands or continua in these two molecules when pure vapour is excited. These diffuse bands or continua also appear analogous to one another and were explained as such by Venkateswarlu.[1–3, 31]

The wavelengths of the bands obtained by Skorko[17] in this region in absorption are also given in the table.

Attempts were made to put all the observed band heads in the vibrational scheme according to the formula suggested by Mathieson and Rees.[15] All the band heads could not be put in the scheme. Further the analysis does not show the proper intensity distribution of the type that is expected for such high v'' values involved according to their formula. It was found that all the bands could be accounted for if the formula given by Venkateswarlu[11] is used along with the Rank's revised constants[13] for the ground state of the molecule. But the intensity distribution is again not of the type that is expected for such involved high v'' values. The intensity distribution of the bands according to both these analyses is quite spasmodic and no proper Frank-Condon parabola could be drawn. It may be pointed out that Wieland and Waser[14] tried to analyse this system using the low v'' values for the ground state, but they could account the bands in the region 3450–3250 Å only and therefore suggested that the rest of the bands in the region 3250–3015 Å may belong to another system. But from the appearance of the bands and their continuity in the region 3460–3015 Å, it is clear that they all most probably belong to one system.

All the bands in the region 3460–3015 Å were found to fit into a single vibrational scheme and could be accounted for fairly well by the formula

$$\nu = 30283 + (103{\cdot}6\ v' - 0{\cdot}095\ v'^2) - (127{\cdot}16\ v'' - 0{\cdot}8356\ v''^2 - 0{\cdot}00108\ v''^3)$$

with $v' = 0$–36 and $v'' = 0$–43. The (v', v'') values and the corresponding (O—C) values calculated from this formula are included in Table I, while the corresponding intensity distribution and the Frank-Condon parabola are shown in Table II. The vibrational constants for the upper state are quite close to those obtained by Venkateswarlu,[11] though the lower state involved according to his analysis is different from the present analysis. The lower state of the system according to this analysis is the $^3\Pi_u$ (O_u^+) state at $T_e = 15642$ cm.$^{-1}$ which forms the upper level of the visible discrete band system of iodine. The vibrational constants of the lower state are those given by Herzberg[18] except that a suitable higher order negative term ($\omega_e y_e$) has been added. These constants give for the lower state the $D_0'' = 4443{\cdot}9$ cm.$^{-1}$ which is quite close to the value of 4439 ± 8 cm.$^{-1}$ calculated from the convergence limit.[18,19]

TABLE I

Wavelengths, wavenumbers and relative intensities of the bands in the system 3460–3015 *Å*

Skorko λ_{air}	Elliott λ_{air}	P.V. λ_{air}	Present experiment I	λ_{air}	λ_{vac}	v', v''	O—C cm.$^{-1}$
			1	3461·0	28885	16, 30	2
			1	59·6	897	7, 19	0
			2	59·1	901	19, 34	−1
			1	57·7	913	14, 27; 17, 31	1, 3
			2	57·4	915	9, 21	−1
			1	56·1	926	10, 22	−2
			3	55·0	935	15, 28	1
	3454·1	3454·4	3	53·9	945	11, 23	3
		52·3	1	52·5	956	12, 24	−1
			1	52·1	959	16, 29	1
		50·2	2	50·3	975	21, 36	2
			2	50·0	977	13, 25	3
	48·2	48·3	5	48·0	994	7, 18	2
			3	47·7	997	14, 26	4
		46·7	4	46·9	29003	8, 19; 20, 34	4, 1
			1	45·2	018	10, 21; 15, 27	0, 5
		44·1	2	43·9	029	11, 22	−1
			1	43·0	036	16, 28; 21, 35	1, 0
		42·0	1	42·4	041	19, 32	2
	41·6		5	41·6	048	12, 23	5
			1	41·1	052	23, 38	2
		40·6	5	40·5	057	17, 29	−1
			2	40·0	061	13, 24	3
		39·7	2	39·3	067	20, 33	−3
	38·9		1	39·0	070	22, 36	−2
		38·1	3	38·2	076	14, 25	1
		37·3	7	36·9	088	2, 12; 3, 13; 5, 15; 6, 16; 7, 17; 18, 30	2, 5, 5, 3, −1, 4
	35·8	36·3	8	35·6	099	0, 10; 8, 18; 15, 26	3, 5, 6
			3	34·9	105	9, 19; 21, 34	4, 3
			4	33·8	114	10, 20; 16, 27; 19, 31	5, 0, 3
			6	33·3	118	11, 21	−1
		32·0	7	32·1	128	26, 42	3
	3431·4		7	3431·3	29135	12, 22; 17, 28; 22, 35	4, 0, −1
		3430·0	7	29·8	148	13, 23	4
			2	29·4	151	24, 38	2
			0	28·5	159	14, 24; 18, 29	0, 0

TABLE I (*Contd.*)

Skorko λ_{air}	Elliott λ_{air}	P.V. λ_{air}	Present experiment I	Present experiment λ_{air}	Present experiment ν_{vac}	v', v''	O—C cm.$^{-1}$
	27·2	27·6	10	27·2	170	21, 33	1
			4	26·8	173	23, 36	2
			3	26·5	176	15, 25	0
			1	26·0	180	26, 41	2
		25·0	6	25·0	189	4, 13; 5, 14; 6, 15; 7, 16; 19, 30	3, 4, 4, 2, 5
		24·0	2	24·5	193	3, 12; 8, 17	4, 2
			2	24·3	195	2, 11; 16, 26	1, 1
			4	23·9	198	9, 18	2
	23·6		7	23·5	201	1, 10; 22, 34	1, 0
		22·9	5	23·0	206	0, 9; 10, 19	−1, 3
			5	22·0	214	11, 20; 17, 27; 20, 31	3, 0, 4
			1	20·9	224	12, 21	3
			0	20·3	229	27, 42	4
			4	19·7	234	13, 22; 26, 40	2, 2
			4	19·6	235	23, 35	0
3419·0		19·1	7	19·2	238	21, 32; 18, 28	−1, 2
	18·8		6	18·6	243	14, 23	−2
		17·5	5	17·6	252	25, 38	4
			4	17·0	257		..
		16·4	3	16·8	259	19, 29	0
			2	16·2	264	15, 24	4
			4	15·8	267	22, 33	−2
		15·4	4	15·4	270	24, 36	0
			1	15·2	273	28, 43	0
			0	14·3	280	16, 25; 27, 41	3, 3
	13·3	13·5	6	13·1	290	4, 12; 5, 13; 6, 14; 7, 15; 8, 16; 20, 30; 26, 39	−2, 1, 2, 2, 1, 6, 1
		12·8	1	12·3	297	9, 17; 17, 26	4, 2
			3	12·1	299	3, 11; 10, 18	2, 1
		11·7	2	11·9	301	23, 34	0
			2	11·7	303	2, 10	0
			1	3411·2	29306	11, 19; 25, 37	2, −2
			1	10·7	311	1, 9; 21, 31;	0, 1
			2	10·1	316	12, 20; 18, 27	4, 2
	3409·7	3409·4	10	09·7	320	0, 8	0
			2	09·4	322	13, 21	0
			3	09·2	324	28, 42	1
			3	08·7	328	27, 40	−3
			3	07·9	335	14, 22; 24, 35	2, 1
			3	07·3	340	19, 28; 22, 32	4, 2

TABLE I (*Contd.*)

Skorko λ_{air}	Elliott λ_{air}	P.V. μ_{air}	Present experiment I	λ_{air}	ν_{vac}	v', v''	O—C cm.$^{-1}$
	06·3	06·3	8	06·3	349	15, 23	3
			9	06·1	351	26, 38	4
		05·7	3	05·3	357	20, 29	−2
			4	05·1	359	16, 24	−2
		04·5	4	04·3	366	23, 33	−2
			3	04·0	369	25, 36	0
3403	03·3	03·1	5	03·2	376	28, 41	1
		02·4	4	02·6	380	17, 25; 21, 30	3, −3
		01·9	6	01·7	389	7, 14; 8, 15; 27, 39	−1, −1, 2
			2	01·2	393	5, 12; 6, 13; 9, 16; 10, 17; 18, 26	−2, 1, 2, −2, −2
	00·6	00·3	10	00·3	401	4, 11; 11, 18; 24, 34	1, 2, 1
		3399·5	6	3399·5	407	3, 10; 12, 19; 26, 37	1, 1, 1
			2	98·9	413	2, 19; 13, 20; 19, 27; 22, 31	−1, 0, −1, 3
			3	98·1	420	29, 42	−1
	3397·8	97·5	2	97·8	422	1, 8	−1
			4	97·3	427	14, 21; 28, 40	4, −2
		95·9	5	96·0	438	0, 7; 15, 22, 20, 28; 23, 32; 25, 35	4, 4, 2, 0, 5
	94·7	94·7	5	94·8	448	16, 23; 27, 38	1, 3
		93·2	2	93·5	460	21, 29	2
			5	93·4	461	17, 24	−1
			4	92·9	465	24, 33; 26, 36	−2, −3
	91·3	91·5	4	91·1	481	18, 25; 22, 30	4, −2
			2	90·0	490	28, 39	4
			2	89·8	492	8, 14; 9, 15	0, 0
			3	3389·6	29494	7, 13; 10, 16	0, 1
	3388·9	3389·0	4	89·0	499	6, 12; 11, 17; 19, 26; 25, 34	2, 3, 4, 0
			7	88·5	503	5, 11; 12, 18; 27, 37	1, 2, −2
			3	88·0	508	4, 10; 13, 19	−1, 1
			1	87·8	509	23, 31	0
			1	86·5	520	3, 9; 14, 20; 30, 42	3, 6, 1
3386		85·6	2	85·6	528	2, 8; 15, 21; 29, 40	1, 4, 0
			1	85·0	533	1, 7; 26, 35	−5, 1
		84·1	2	83·7	545	17, 23; 28, 38	−2, 1
	82·9	82·2	4	82·8	553	0, 6	3
	81·2	81·5	1	81·9	561	22, 29	3
			1	81·3	566	18, 24; 25, 33; 27, 36	4, 0, −1

TABLE I (*Contd.*)

Skorko λ_{air}	Elliott λ_{air}	P.V. λ_{air}	Present experiment I	λ_{air}	ν_{vac}	v', v''	O—C cm.$^{-1}$
			1	79·8	579	19, 25	2
		79·6	4	79·5	582	29, 39	−2
	79·2		7	79·3	584	23, 30	2
			2	78·0	595	10, 15; 11, 16	1, 0
			2	77·8	596	8, 13; 9, 14; 20, 26	0, 2, 1
			2	77·5	599	12, 17; 26, 34	1, 1
	77·0	77·3	3	77·1	602	7, 12; 28, 37	2, −1
			4	76·9	604	13, 18	2
			7	76·7	606	6, 11	1
			1	76·1	612	5, 10; 14, 19; 24, 31	0, 4, 4
			1	75·7	615	15, 20; 21, 27; 31, 42	0, 1, −2
		74·5	3	74·5	625	4, 9; 16, 21; 30, 40	5, 0, −1
	74·1		3	74·3	628	3, 8; 27, 35	−2, −3
			3	73·3	636	17, 22; 22, 28; 25, 32	1, 1, 0
			1	73·0	639	2, 7	−2
			3	72·1	647	18, 23; 29, 38	−1, 5
	71·6	71·8	5	71·3	654	1, 6; 23, 29	0, −3
			1	70·2	663	19, 24; 26, 33	1, −2
3369	69·7	69·2	3	69·4	670	0, 5	2
			1	69·2	672	31, 41	3
		67·9	1	67·9	684	20, 25	7
	67·6		4	67·6	686	24, 30	5
			7	3367·4	29688	30, 39	6
		3366·4	1	66·8	693	11, 15	−2
			3	66·5	696	9, 13; 10, 14; 12, 16; 21, 26; 27, 34	−2, 0, 0, 1, 0
			3	65·8	702	8, 12; 13, 17; 29, 37	0, 3, 0
		65·2	5	65·4	706	7, 11; 14, 18; 25, 31	−1, 3, −1
		63·8	3	63·8	720	5, 9; 31, 40	−3, −3
	3362·6	62·4	3	62·6	731	17, 21; 28, 35	6, 2
			2	62·2	734	4, 8	1
			0	62·0	736	23, 28; 26, 32	2, 1
			2	61·5	740	18, 22; 30, 38	4, 0
		60·7	2	60·9	746	3, 7	2
	59·9	59·1	5	60·0	753	19, 23	5
			5	59·7	756	2, 6	−1
			0	59·1	761	24, 29	5
		58·6	5	58·9	763	20, 24; 27, 33; 29, 36	1, −1, 0
	57·9	57·8	6	57·7	774	1, 5	2
			0	57·1	779	21, 25; 31, 39	2, −1

TABLE I (*Contd.*)

Skorko λ_{air}	Elliott λ_{air}	P.V. μ_{air}	Present experiment I	λ_{air}	ν_{vac}	v', v''	O—C cm.$^{-1}$
	56·0	56·3	0	56·4	785	25, 30	5
			2	55·8	791	0, 4	3
			0	55·4	794	22, 26	0
			0	55·2	796	12, 15; 28, 34	−1, 1
			0	54·9	799	11, 14; 13, 16	1, 2
			0	54·7	800	10, 13; 14, 17; 30, 37	0, 0, 0
	54·3	54·2	4	54·1	806	9, 12; 15, 18; 26, 31	2, 2, 0
			0	53·3	813	8, 11; 16, 19; 23, 27	4, 4, 0
3353		53·0	2	52·9	816	7, 10	−1
			1	52·5	820	17, 20	3
		52·3	1	52·3	822	32, 40	1
			?	51·9	825	18, 21	0
		51·0	1	51·1	832	19, 22; 24, 28; 27, 32	−4, −1, −1
			?	50·4	839	5, 8; 31, 38	4, 2
		49·8	1	49·6	846	4, 7	−1
			0	48·9	852	20, 23	4
	48·1	48·2	1	48·3	857	25, 29	2
			5	3347·9	29861	3, 6; 30, 36	1, 0
			0	47·5	865	21, 24; 28, 33	4, 3
			0	46·8	871	22, 25	−6
	3346·4	3346·2	6	46·2	876	2, 5; 32, 39	1, −1
			?	45·6	882	26, 30	3
			0	44·5	891	1, 4; 23, 26; 29, 34	0, −2, −2
			?	43·7	899	12, 14; 13, 15; 31, 37	0, 1, 2
		43·4	1	43·4	901	11, 13; 14, 16; 15, 17	−1, 3, 0
			0	43·1	904	10, 12; 16, 18; 27, 31	−2, 0, 0
			0	42·4	910	0, 3	1
		42·0	0	42·1	913	9, 11; 17, 19; 24, 27	2, 3, 1
			1	38·6	944	6, 8	6
3339		38·4	3	38·3	947	21, 23	0
			1	37·9	950	5, 7	0
			0	37·7	952	26, 29	−2
			0	36·8	960	31, 36	1
	36·5	36·7	5	36·5	963	29, 33; 34, 41	3, 2
			3	36·3	965	4, 6	2
			0	36·0	967	22, 24	6
			0	35·5	972	33, 39	−3

TABLE I (*Contd.*)

Skorko λ_{air}	Elliott λ_{air}	P.V. μ_{air}	Present experiment I	λ_{air}	ν_{vac}	v', v''	O—C cm.$^{-1}$
	34·9	35·3	4	34·9	977	23, 25	1
			2	34·7	979	3, 5	1
			0	34·4	982	27, 30	4
			3	33·6	989	30, 34	−2
		33·3	2	33·3	992	2, 4; 24, 26	−3, −1
			0	32·9	995	32, 37	0
		31·9	2	32·0	30003	12, 13; 13, 14; 14, 15; 15, 16	0, 3, 4, 4
			2	31·6	007	11, 12; 17, 18	0, 2
			1	31·1	012	1, 3	−1
		30·1	0	30·8	014	10, 11	1
			1	30·0	021	9, 10	0
		29·2	2	29·0	030	0, 2; 8, 9	−2, 0
3327		3327·9	4	3328·0	30039	7, 8	−1
			?	26·7	051	6, 7	−1
		25·6	6	25·0	067	5, 6	1
		24·8	2	24·5	071	34, 39	−1
		24·2	2	24·0	076	24, 25	1
			2	23·5	080	4, 5	−1
			0	22·7	087	31, 34	−2
			5	21·7	096	3, 4	−2
			2	20·8	105	13, 13; 14, 14	1, 4
			0	19·9	113	11, 11; 12, 12; 2, 3	−2, 4, −3,
			?	18·8	123	10, 10	0
			1	18·0	130	9, 9	−2
		17·6	3	17·5	135	1, 2	−1
		16·3	2	16·2	146	8, 8	4
		15·6	4	15·3	155	0, 1; 7, 7	−2, 0
		13·9	6	13·7	169	6, 6	1
			?	11·8	186	5, 5	2
		11·1	0	10·5	198	4, 4	−3
			0	09·7	206	14, 13; 15, 14	1, 4
3309		09·0	0	09·3	209	13, 12	−1
			0	08·8	214	12, 11	−2
			0	08·0	221	3, 3	2
		07·1	1	07·1	229	11, 10	5
		05·8	?	05·6	243	2, 2	4
		04·3	6	03·8	259	1, 1; 8, 7	−1, 2
		03·0	3	02·9	268	7, 6	−3
		02·1	3	02·8	270	30, 30	−2
			0	01·2	283	0, 0; 6, 5	0, −3
		00·2	2	3299·9	295	27, 26	6
			1	99·7	297	31, 31	0

TABLE I (*Contd.*)

Skorko λ_{air}	Elliott λ_{air}	P.V. μ_{air}	Present experiment I	λ_{air}	ν_{vac}	v', v''	O—C cm.$^{-1}$
		3299·0	1	99·2	302	17, 15	1
			1	99·0	303	5, 4	0
			1	98·9	304	16, 14	1
			0	98·5	308	15, 13	2
			?	3297·8	30315	14, 12	4
			0	97·0	322	4, 3; 13, 11	0, 5
		3296·2	3	96·4	327	12, 10	1
3295			1	95·7	334	11, 9	−1
			0	94·9	341	3, 2	−1
		94·1	4	94·2	348	10, 8	2
			0	93·6	353	30, 29	6
		92·6	6	92·8	361	26, 24	4
			1	92·5	363	9, 7	4
			3	92·3	365	2, 1	1
			0	91·8	370	31, 30	0
		91·1	1	91·1	376	27, 25	5
			1	90·9	378	8, 6	5
		90·0	3	90·1	385	34, 34	4
			1	89·7	389	1, 0; 7, 5; 28, 26	2, 0, 2
		88·5	3	88·6	399	19, 16	−2
			2	88·2	403	17, 14	0
			0	87·8	407	6, 4	1
		87·0	0	87·5	410	15, 12; 16, 13	−2, 3
		86·1	1	86·4	420	14, 11	2
			1	86·2	422	24, 21	−1
			1	86·0	424	5, 3	−1
		85·0	2	84·9	433	13, 10	6
3283		84·0	0	84·2	440	12, 9	3
			3	83·9	443	4, 2	−2
		82·2	4	82·2	458	27, 24	2
			4	81·9	462	10, 7	1
			0	81·5	469	3, 1	2
		79·9	3	80·0	479	9, 6	4
			3	79·6	483	29, 26	−3
			0	78·8	490	2, 0	0
		78·6	1	78·6	492	8, 5	1
		78·0	2	77·9	499	20, 16	−2
			2	3277·7	30500	19, 15	−1
			1	77·5	502	18, 14	−2
		3276·6	1	76·8	509	7, 4; 17, 13	1, 2
			1	75·8	518	15, 11; 16, 12	−1, 5
		74·7	0	74·6	529	6, 3; 14, 10	2, 1

TABLE I (*Contd.*)

Skorko λ_{air}	Elliott λ_{air}	P.V. μ_{air}	Present experiment I	λ_{air}	ν_{vac}	v', v''	O—C cm.$^{-1}$	Skorko λ_{air}
3273			1	73·5	540	13, 9	2	3238
			0	72·9	545	5, 2	−3	
		71·7	4	71·8	555	12, 8; 28, 24	6, 1	
		71·2	4	71·1	562	11, 7	0	
			2	70·0	572	4, 1	3	
		69·5	1	69·6	576	10, 6	−1	
			3	68·8	583	30, 26	−1	
			1	68·2	589	3, 0	−4	
		67·6	1	67·6	595	9, 5	2	
			0	67·2	599	21, 16	−2	
			3	65·8	611	8, 4; 18, 13	0, 3	
			0	65·4	615	17, 12	2	
			0	65·0	619	16, 11	−1	3228
		64·5	3	64·5	624	15, 10	−5	
3263		63·4	3	63·5	633	7, 3	3	
		62·2						
		61·8	3	61·8	649	6, 2	−1	
			0	61·2	655	13, 8	5	3219
		60·9	1	60·8	659	29, 24	7	
			0	59·9	667	30, 25; 12, 7	1, 3	
		59·6	1	59·6	670	5, 1	−2	
		58·9	2	58·3	682	31, 26; 11, 6	1, 4	
		57·9	2	57·5	690	10, 5	−5	
			0	57·1	693	4, 0	−3	
		56·2	1	54·9	714	9, 4; 18, 12	1, 1	3211
3253		53·6	1	53·3	729	16, 10	0	
			0	52·5	737	8, 3	5	
			2	52·1	740	29, 23	2	
		51·4	2	51·6	745	15, 9	5	
		3251·4	3	3250·7	30754	7, 2; 14, 8; 30, 24	1, 3, 4	
		49·4	1	48·9	771	13, 7	6	
		48·4	?	48·5	775	6, 1	0	
3245		45·7	0	46·0	799	5, 0; 11, 5	0, 3	
			1	45·3	805	20, 13	−3	3199
			0	44·1	816	10, 4	2	
		43·6	0	43·2	825	18, 11	4	
		41·9	?	42·2	834	9, 3; 17, 10	0, 4	
			0	41·7	839	16, 9	−1	
	3240·6	40·9	3	40·7	849	31, 24	1	
			2	40·4	851	15, 8	−1	
		39·7	0	39·8	857	8, 2	2	3188
			0	38·4	870	14, 7	4	

TABLE I (*Contd.*)

Skorko λ_{air}	Elliott λ_{air}	P.V. λ_{air}	Present experiment I	λ_{air}	ν_{vac}	v', v''	O—C cm.$^{-1}$
3238	37·5	37·7	1	37·6	878	7, 1	1
		36·2	0	36·5	889	13, 6	8
			1	36·0	893	12, 5	−5
	34·6	34·8	2	34·8	905	6, 0	4
		33·7	1	33·8	915	11, 4; 20, 12	−1, 2
		32·1	1	32·3	929	30, 22	−5
			1	31·8	934	18, 10	4
			1	31·3	939	10, 3	3
			0	31·0	941	17, 9	0
	29·9	30·2	3	30·1	950	16, 8	−3
			?	29·5	956	9, 2	−1
		28·8	1	28·7	963	15, 7	−4
3228		27·7	0	27·9	971	8, 1	−8
			0	26·3	986	14, 6	4
	24·3	24·3	0	24·3	31006	7, 0	2
	22·2	22·7	1	22·7	021	12, 4; 20, 11	4, 0
	19·9	20·4	?	20·3	044	11, 3; 18, 9	7, 3
3219			3	19·2	055	10, 2; 17, 8	−4, 1
		18·1	1	18·1	065	16, 7	−2
		17·1	1	16·8	078	9, 1	−3
	14·3	14·5	3	14·3	102	8, 0; 25, 15; 24, 14; 14, 5	−4, 4, 1, 2
		3213·5	0	3213·0	31115	13, 4; 22, 12	−4, 2
	3211·9	12·2	3	12·0	124	21, 11	3
3211		10·8	1	10·8	136	12, 3; 20, 10	−3, 6
	09·7	09·6	4	09·3	150	18, 8	−4
		08·6	3	08·4	159	11, 2	−1
			0	07·1	172	17, 7	4
			1	06·0	183	16, 6; 10, 1	−1, 0
		03·1	2	03·6	206	9, 0; 15, 5; 24, 13	−2, 5, 1
			1	02·9	213	23, 12	1
			?	01·9	223	14, 4; 22, 11	3, 3
			?	00·6	235	21, 10	5
3199	3199·9	00·1	2	3199·9	242	13, 3; 20, 9	2, 1
			1	99·1	250	19, 8	−4
	97·1	3197·7	2	97·6	264	12, 2	2
		95·2	0	94·8	291	11, 1	6
		93·0	?	93·4	306	16, 5; 25, 13	4, 2
			0	92·8	312	10, 0; 24, 12	2, 1
		91·7	2	91·8	321	15, 4; 23, 11	1, 2
3188	89·3	89·7	?	89·7	342	14, 3	1
			2	89·2	347	21, 9	6
			0	88·6	353	20, 8	1
			0	87·2	366	13, 2; 19, 7	3, −2

TABLE I (*Contd.*)

Skorko λ_{air}	Elliott λ_{air}	P.V. μ_{air}	Present experiment I	λ_{air}	ν_{vac}	v', v''	O—C cm.$^{-1}$
	84·8	84·7	0	85·3	385	18, 6	1
			2	84·9	389	12, 1	3
		82·7	0	82·8	410	11, 0; 25, 12	−1, 0
		81·7	1	81·4	424	16, 4; 24, 11	3, 6
3180		80·3	0	81·2	426	23, 10	−3
	78·8	79·1	2	79·0	447	15, 3; 22, 9	5, 7
		77·6	1	77·6	461	14, 2	−3
			?	77·2	465	20, 7	−3
			0	75·0	487	13, 1; 19, 6	0, 2
			2	73·3	504	18, 5; 27, 13	2, 2
	72·8	73·1	0	73·0	507	26, 12	−2
			0	3171·6	31521	25, 11	4
			0	71·2	525	17, 4	3
3171	3169·6	3169·9	2	69·6	541	23, 9	1
			1	68·9	548	16, 3	6
		67·6	0	67·5	561	15, 2	−4
		66·8	0	67·0	569	21, 7	1
	65·7	66·0	0	65·7	579	20, 6	−5
		64·4					
		63·4	0	63·2	604	19, 5; 28, 13	2, 4
		62·3					
3161		61·2	0	61·2	625	18, 4; 25, 10	3, −2
		60·0	3	60·0	636	24, 9	−3
	59·2	59·5	3	59·2	644	17, 3	1
			0	58·5	651	23, 8	−1
			?	56·8	669	22, 7	2
		54·8	0	54·5	692	15, 1	3
3151		51·7	0	51·3	724	19, 4	2
	49·5	50·4	2	49·5	739	25, 9	1
			0	48·5	752	24, 8	1
			1	47·5	762	17, 2	−4
	46·4	46·7	1	46·6	771	23, 7	4
		42·3				28, 11	2
3141	40·2	40·6				26, 9	−5
	36·9	37·1				24, 7	1
		34·0				31, 13	5
	33·4	33·2				22, 5	5
3132	30·6	30·9				28, 10	7
	28·5	28·6				26, 8	5
		27·9				25, 7	−4
	24·3	24·9				32, 13	0
3123	21·0	21·4				28, 9	−6
		19·4				27, 8	0
		18·5				26 ,7	−7

TABLE I (*Contd.*)

Skorko λ_{air}	Elliott λ_{air}	P.V. μ_{air}	Present experiment I	λ_{air}	ν_{vac}	v', v''	O—C cm.$^{-1}$
		3117·5				20, 2	2
		16·3				25, 6	−1
3112	3111·4	13·1				31, 11	6
3105		05·3				25, 5	−5
		04·1				32, 11	1
		3099·9				29, 8	−6
3095	3097·9	96·4				21, 1	−4
		92·7				25, 4	6
	89·2	88·1				28, 6	−4
3084	85·5	83·8				26, 4	1
		82·2				25, 3	−5
		81·1				31, 8	−7
3076	75·1	75·9				35, 11	−5
3067	65·9	67·3				29, 5	0
3059	57·3	58·9				25, 1	−5
3052	53·4	53·7				28, 3	2
	48·5	48·7				31, 5	2
		45·3				29, 3	−6
3042		43·0				28, 2	−6
	40·4	40·5				27, 1	−5
3035		37·8				31, 4	1
		32·8				34, 6	0
3029		27·3				31, 3	−7
		19·7				28, 0	−4
		14·6				36, 6	5

Note.—The bands assigned in the above table between 3146–3014 Å are those which were measured by Venkateswarlu.[11] Their positions are shown by × in Table II. These bands are weak and therefore are not recorded with the grating spectrograph in the present experiments.

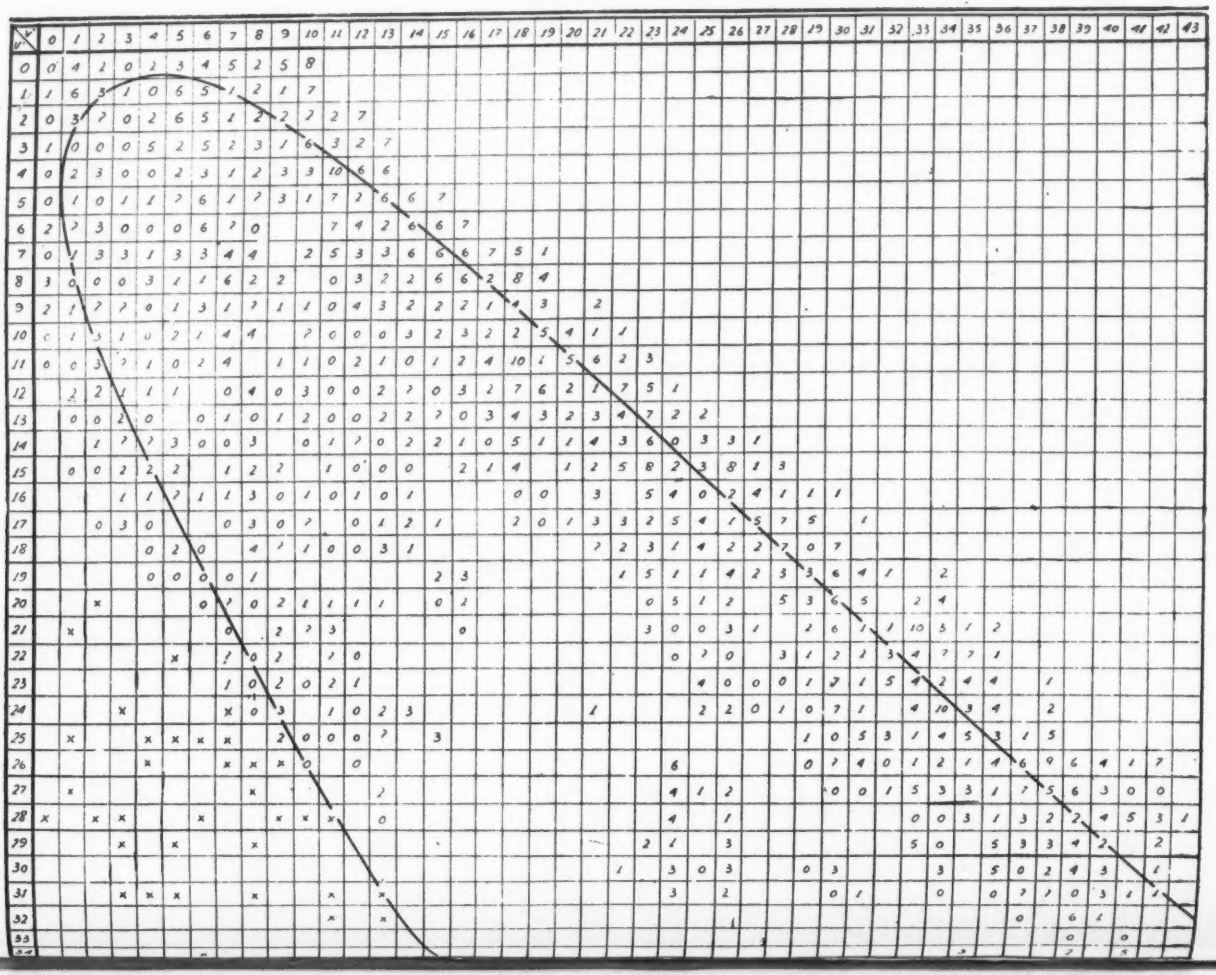
This analysis of the 3460–3015 Å system of iodine is thus analogous to that of the 2950–2670 Å system of bromine which was supported by the proper corresponding intensity distribution and the probable observed isotopic shifts.

THE BAND SYSTEM 4420–4000 Å

No further work has been done on this system than was done by earlier workers. The band system obtained by Elliott[9] in fluorescence in the region 4321–4041 Å had been extended by Venkateswarlu[11] to the region 4420–4000 Å using transformer discharge in the presence of argon. According to Wieland and Waser[14] and also Venkateswarlu the lower state of the

TABLE II

The intensity distribution and Frank-Condon parabola of the band system 3460–3015 *Å of iodine*



system is the $^3\Pi_u$ (O_u^+) state at $T_e = 15642$ cm.$^{-1}$ The upper state is at $T_e' = 41411$ cm.$^{-1}$ with $\omega_e' = 102{\cdot}2$ cm.$^{-1}$ The analysis of this system shown in Venkateswarlu's paper gives the Frank-Condon parabola of the expected type. The band system 3150–2970 Å of bromine, obtained and discussed recently by Venkateswarlu and Verma,[20] appears to be analogous to this system of iodine.

The Band System 2785–2731 Å

This weak system was photographed on the first order 21-ft. grating spectrograph and is shown in Fig. 2. The wavelengths and wavenumbers of the band heads along with their visually estimated relative intensities are given in Table III. The wavelengths of the band heads given by Venkateswarlu[11] are also included in Table III for comparison. One can see from

Table III

Wavelengths, wavenumbers and relative intensities of the bands in the system 2785–2731 Å

P.V.	Present experiment			P.V.	Present experiment		
λ_{air}	I	λ_{air}	ν_{vac}	λ	I	λ_{air}	ν_{vac}
2784·5	0	2784·9	35897	2758·6	1	2758·6	36240
	0	83·4	917	57·5	2	57·5	254
	?	81·1	946	56·1	2	56·4	269
79·8	5	79·6	966		3	55·9	275
	1	78·4	981	55·0	2	55·1	286
	1	77·4	994		0	54·3	296
76·0	2	75·8	36015		1	52·9	314
75·3				50·7	1	51·6	332
74·6	2	74·6	031		2	49·2	363
73·2	2	73·6	044		2	48·9	367
72·1	6	72·2	062	48·3	2	48·1	378
71·4	2	71·2	075		1	46·5	400
70·3	2	70·4	085		2	45·3	415
69·4	4	69·4	098		2	45·0	419
68·7	2	68·5	110		2	44·4	427
68·3	4	67·8	119		?	42·6	451
67·3	1	67·2	127		1	41·3	468
	1	66·7	133		1	40·1	484
65·4	2	65·3	152		0	39·4	494
64·1	2	64·3	165		0	38·9	500
	2	63·7	173		1	36·7	530
62·8	2	63·0	182		1	35·6	544
62·4	2	62·4	190		1	34·5	559
61·5	4	61·7	199		1	33·2	576
60·1	2	60·0	221		0	32·3	588
59·3	1	59·3	230		0	30·9	607

the table that a number of new bands are obtained in the present experiments. The region 2785–2748 Å of the band system obtained by Venkateswarlu has been extended here to the region 2785–2731 Å.

The Deslandres scheme of the bands is shown in Table IV. The $\triangle G''(v+\frac{1}{2})$ values are such that they can be represented by the ground state

TABLE IV

The vibrational analysis of the band system 2785–2731 *Å of iodine*

v'' / v'	0	1	2	3	4	5	6	7	8	9	10	11	12	13	$\Delta G(v''+\frac{1}{2})$ obs	$\Delta G(v''+\frac{1}{2})$ cal
0	36199	36075	35946												112·6	111·0
	129 115	129 107	116													
1	36314	36182	36062												107·3	107·6
	132 105	120 114	103													
2	36419	36296	36165	36044											108·3	108·3
	123 111	131 109	110	108												
3	36530	36400	36275	36152	36031	35917									101·0	106·9
	130 100	125 103	123 102	121 102	114 98											
4	36500	36378	36254	36133	36015										106·6	105·6
	122 107	124 106	121 109	118 107	104											
5	36607	36484	36363	36240	36119			35897							104·3	104·3
	123 104	121 105	123 111	121 97												
6	36588	36468		36230	36110			35994							106·3	103·0
	120 108	120 102	111	116 104												
7	36576	36451	36332	36227	36098	35981									98·3	101·8
	127 93	119 95	111 101	123 104												
8	36594	36427		36199	36085										104·0	100·6
	117 103	114 105														
9	36530	36415		36190	36075	35966									98·2	99·4
	115 103	115 96	115 98	109 96												
10	36518	36400	36286	36173	36062										95·0	98·2
	118 94	114 96	113 98	111												
11	36494	36269													98·0	97·1
	98															
12	36367															96·0
														36031		
13														96	96	94·9
14										36559				36127		
$\Delta G(v''+\frac{1}{2})$ obs.	127·2	125·0	121·6	123·0	117·8	115·3	119·0	115·0	114·0	110·0						
$\Delta G(v''+\frac{1}{2})$ cal.	126·3	124·6	123·0	121·3	119·6	117·9	116·2	114·9	112·7	111·0						

with $v'' = 53$ to $v'' = 62$ or by the $^3\Pi_u$ (O_u^+) level at $T_e = 15642$ cm.$^{-1}$ with $v'' = 0$ to $v'' = 13$. The Frank-Condon parabola of the intensity distribution, that one gets, favours the lower state to be the $^3\Pi_u$ (O_u^+) state and not the ground state of the molecule. It was found that all the bands in the system could be well represented by the formula.

$$\nu = 36197 + (111{\cdot}7\,v' - 0{\cdot}705\,v'^2 + 0{\cdot}004\,v'^3) - (127{\cdot}16\,v'' - 0{\cdot}8356\,v''^2 - 0{\cdot}00108\,v''^3)$$

with $v' = 0$–14 and $v'' = 0$–13.

The band system according to the analysis is due to a transition from an upper state with $T_e = 51846$ cm.$^{-1}$ The lower state is the $^3\Pi_u$ (O_u^+) state and is common to the band system 4420–4000 Å and 3460–3015 Å. The intensity distribution corresponding to the present analysis is shown in Table V. This system is probably analogous to the weak system 2660–2590 Å of bromine obtained and discussed by Verma.[21] It may be remarked that this system was not observed in fluorescence by Elliot[9] probably because this is extremely weak compared to the other systems obtained in fluorescence.

The Band System 2730–2486 Å

The wavelengths and wavenumbers of the band heads as measured from the plates taken on the first order 21-ft. grating sepctrograph are given in Table VI. The wavelengths of the band heads obtained by Elliott[9] along with those obtained by Venkateswarlu[11] in the transformer discharge using the Hilger E_1 Littrow quartz spectrograph are also included in Table VI. A number of new bands are recorded in the present experiments in the region studied by the previous workers and also the system is extended on the short wavelength side from 2520–2486 Å. To account for all the bands the band system was reanalysed and Deslandres scheme is given in Table VII with the corresponding intensity distribution in Table VIII. The Frank-Condon parabola of intensity distribution can be seen to be of the expected type. It was found that all the bands could be well represented by the formula

$$\nu = 47148 + (96{\cdot}0\,v' - 0{\cdot}505\,v'^2 + 0{\cdot}0033\,v'^3) - (213{\cdot}6396\,v'' - 0{\cdot}60936\,v''^2 - 1{\cdot}3119\times10^{-3}\,v''^3 - 5{\cdot}2386\times10^{-6}\,v''^4 - 1{\cdot}81665\times10^{-7}\,v''^5 + 5{\cdot}555\times10^{-10}\,v''^6)$$

with $v'' = 41$–70 and $v' = 0$–10. The vibrational constants and the position of the upper level are only slightly different from those of the earlier workers. The lower state of the system is the ground state of the molecule. The constants used in the equation of the ground state are those of Rank and Baldwin[13] except that their last two negative terms are slightly changed and

a suitable higher order positive term is added. This slight modification of their constants is justified because they obtained the constants from the resonance data corresponding to the vibrational levels upto $v'' = 36$ only whereas the v'' involved in the present analysis ranges from $v'' = 41$ to $v'' = 70$. The modification is made in such a way that the present equation for the ground state explains Rank and Baldwin's experimental data[22] well

TABLE V

The intensity distribution and Frank-Condon parabola of the band system 2785–2731 Å

v'/v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	6	2	?											
1	1	2	2											
2	2	0	2	2										
3	1	1	3	2	2	0								
4		0	2	2	1	2								
5		0	1	2	1	5		0						
6			0	1		1	2	1						
7				1	?	1	2	4	1					
8					2	2		4	2					
9						1	2		2	2	7			
10							1	1	1	2	8			
11								0		2				
12										2				
13														2
14										1				1

TABLE VI

Wavelengths, wavenumbers and relative intensities of the bands in the system 2730–2486 *Å*

Elliott λ_{air}	P.V. λ_{air}	Present experiment		
		I	λ_{air}	ν_{vac}
	2729·1	0	2728·9	36634
2727·4		0	27·2	657
		0	21·7	731
20·7	20·6	6	20·6	746
		1	19·6	759
		0	19·0	767
		2	17·1	793
		1	15·2	819
	14·9	2	14·8	824
14·2		3	14·3	831
		6	14·0	835
	13·8	2	13·3	845
		1	12·5	855
	11·7	1	11·7	866
	09·7	1	10·6	881
		1	08·6	909
	07·6	2	07·5	924
	06·3	1	06·6	936
		3	05·3	954
04·7	04·9	2	04·7	962
03·6	03·5	3	03·6	977
02·5	02·5	2	02·2	996
		3	2699·0	37040
	2697·8	1	97·6	059
96·6	96·7	4	96·7	071
95·4	95·5	4	95·5	088
		1	94·8	098
94·4	94·2	3	94·2	106
	89·1	4	88·6	183
87·3	87·6	4	87·3	201
86·0	85·9	3	85·9	220
		0	84·5	240
		0	81·6	280
		0	80·6	294
2679·0	2679·0	4	2679·0	37316
77·4	77·5	4	77·4	339
	76·3			
	75·4	1	75·4	367
		1	74·0	386
		1	72·4	408
	71·2	2	70·5	435

TABLE VI (*Contd.*)

Elliott λ_{air}	P.V. λ_{air}	Present experiment		
		I	λ_{air}	ν_{vac}
68·7	68·9	5	68·7	460
		?	67·8	473
		?	66·6	490
65·7	65·7	0	65·6	504
64·0	64·1	0	63·7	531
	62·3	2	62·0	555
		5	61·1	567
60·0	60·2	4	60·1	581
	57·9	1	57·4	620
		2	56·1	638
55·3	55·5	2	55·3	649
	51·7	?	52·7	686
51·2	51·3	4	51·2	708
	48·5	0	48·6	748
46·5	46·7	1	46·5	775
44·6	45·0	2	44·4	805
42·3	42·3	4	42·2	836
	40·5	3	40·2	865
37·9	38·5	?	38·3	892
35·6	35·7	3	35·5	932
33·2	33·5	3	33·2	965
	31·4	2	31·5	990
	29·4	1	29·1	38024
26·7	26·9	3	26·6	061
24·2	24·1	2	24·0	098
22·7	22·7	1	22·6	119
		2	20·0	157
2617·6	2617·6	3	2617·5	38193
	16·1	1	16·5	208
14·9	15·0	2	14·7	234
	13·6	0	13·4	253
		1	12·5	266
11·3	11·2	1	10·9	290
08·3	08·4	3	08·3	328
	07·4			
05·7	05·4	3	05·5	369
	04·0	1	03·9	392
01·9	02·0	3	01·9	422
2599·1	2599·3	3	2599·0	465
96·5	96·5	1	95·9	511
		2	94·2	536
92·9	92·9	2	92·6	560
89·9	89·8	2	89·6	604

TABLE VI (*Contd.*)

Elliott λ_{air}	P.V. λ_{air}	Present experiment		
		I	λ_{air}	ν_{vac}
86·6	87·0	1	86·6	649
83·4	83·4	3	83·3	699
80·3	80·6	2	80·1	747
77·2	77·4	2	77·1	792
74·1	74·3	2	74·0	838
70·8	70·8	1	70·7	888
67·9	67·8	2	67·8	932
64·6	65·1	2	64·5	982
61·6	62·1	1	61·9	39026
58·4	58·8	2	58·3	076
55·1	55·4	1	55·1	126
52·4	52·4	1	52·3	169
48·9	49·3	1	48·9	221
	46·5			
45·4	45·4	0	45·4	275
43·0	43·1	1	43·2	309
39·4	39·5	1	39·6	364
33·5	33·7	1	33·4	460
		1	2530·1	39512
		1	27·6	551
2524·2	2524·2	1	23·8	609
		0	20·5	663
		0	18·1	701
		?	15·9	735
13·9	13·9	2	14·3	761
		0	12·2	791
		0	08·6	851
		1	04·8	910
		1	02·9	942
		0	2499·2	40001
		?	93·3	095
		0	91·3	128
		0	87·9	182
		?	86·1	212

and at the same time gives $\triangle G''(v + \frac{1}{2})$ values close to those obtained in the present analysis. It is to be mentioned that Rank and Baldwin's constants give $D_0'' = 12021$ cm.$^{-1}$ for the dissociation energy whereas the present constants give $D_0'' = 12249$ cm.$^{-1}$ which is close to the accurate value of 12439 ± 8 cm.$^{-1}$ known from the convergence limit[18, 19] of the visible absorption band system. It is probable that there may be still certain positive terms of higher order involved which will become appreciable above $v'' = 70$ and

TABLE VII

The vibrational analysis of the band system 2730–2486 Å of iodine

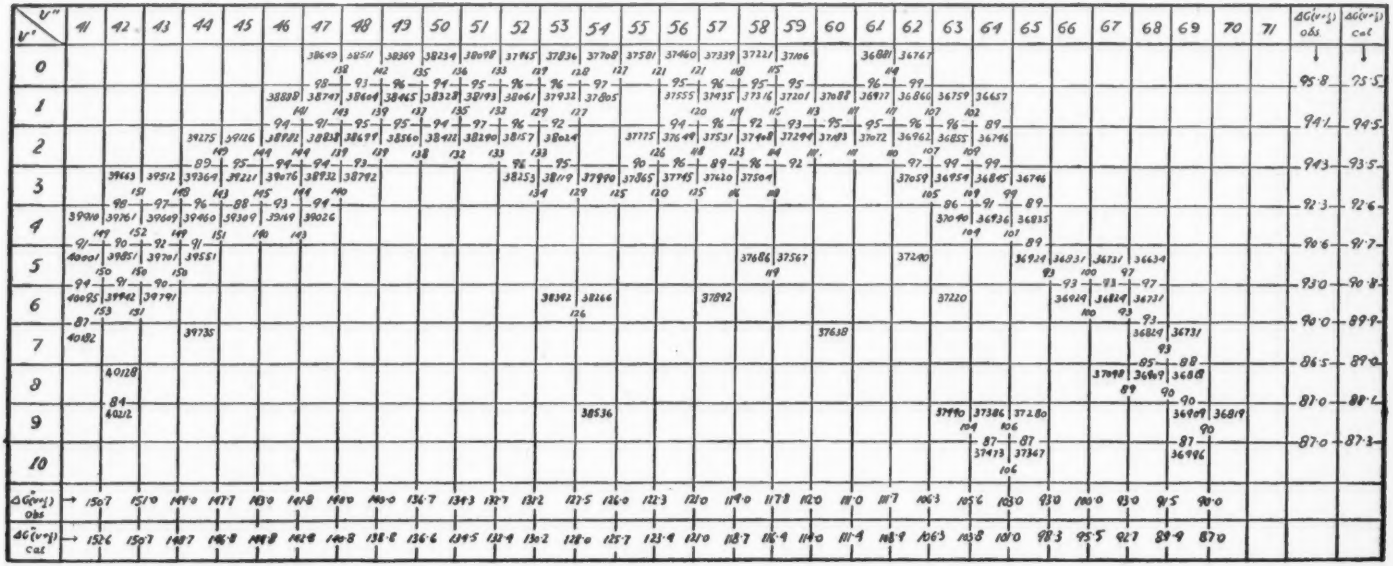


TABLE VIII

The intensity distribution and Frank-Condon parabola of the band system 2730–2486 *Å of iodine*

v'/v''	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
0							0	2	3	2	2	3	1	1	1	5	1	3	3		1	6									
1						1	2	2	3	3	3	3	3	2		2	2	4	4	4	3	1	1	0							
2				1	1	2	2	3	3	3	1	3	1		1	2	0	1	2	4	4	2	1	6							
3		0	0	1	1	2	2	2				0	1	2	3	0	1	0	1			1	3	2	6						
4	0	0	0	1	1	1	0																3	1	6						
5	0	0	0	?														?	5			0			2	3	0	0			
6	?	1	1										1	1			?						0			2	2	0			
7	0			?																2								2	0		
8		?																									1	1	1		
9		?												2									?	1	0				1	1	
10																								?	1				2		

which may take the dissociation limit to 12439 ± 8 cm.$^{-1}$, the value obtained from the convergence limit.

It is to be mentioned that in bromine, the band system corresponding to the 2730–2486 Å of iodine is not yet observed and might lie in the shorter wavelength region than that investigated till now.

Remarks on the Absorption Data in the Quartz Ultra-Violet Region

Pringsheim and Rosen[23] obtained bands in the region 2760–2090 Å, using temperatures in the range 200–800° C with a pressure of about one atmosphere. Kimura and Miyanishi[24] extended the absorption data to the region 2150–1950 Å using temperatures in the range 35–120° C.

Skorko[17] working in absorption at high temperatures obtained at a temperature of 775° C. a continuum at 3413 Å and at a temperature of 885° C. another continuum at 3263 Å. By further increasing the temperature upto 1050° C. he found that diffuse narrow bands appear overlapping the continua. He gave the wavelengths of these bands in the region 3419–2974 Å and did not mention that they unite with P-R bands on the short wavelength side. The wavelengths of these bands in the region 3419–3150 Å as given by Skorko are included in Table I for comparison with the emission bands in that region.

Warren[25] investigated the absorption spectrum at different temperatures upto 1100° C. He suggested that the P-R and K-M bands belong to one system. By increasing the temperature he obtained like Skorko two continua with intensity maxima at 3413 Å and 3263 Å. By a further increase of temperature he finds at 1115° C. that the absorption bands increase towards longer wavelengths and ultimately reach 3413 Å overlapping the two continua. He did not give the measurements of the absorption bands or their analysis, but was of the opinion that all the bands in the quartz ultra-violet belong to one system.

Venkateswarlu[26] analysed the bands obtained by Pringsheim and Rosen[23] and Kimura-Miyanishi[24] into one system but $\triangle G\,(v+\frac{1}{2})$ values obtained were so spasmodic that no formula could be developed. By long extrapolation the position of the upper level was extrapolated to be 44900 cm.$^{-1}$ He was of the opinion that Skorko bands belong to a different transition from that of the P-R and K-M bands.

Mathieson and Rees[15] are of the opinion that the P-R, K-M and the Skorko bands along with the continuum at 3413 Å and the emission bands in the region 3450–3040 Å belong to one and the same transition with the

ground state of the molecule as the lower state. It is difficult to accept this view, because Skorko's as well as Warren's observations show that the continuum at 3413 Å appears first at 800° C., and then at about 1050–1150° C. this continuum is overlapped by the Skorko bands. If the continuum at 3413 Å belongs to the same transition as the Skorko bands and forms the long wavelength limit of these bands, the Skorko bands should appear first and then the continuum with further increase of temperature. A continuum at 3416 Å, which is obviously identical with that in absorption, occurs in both electrical and fluorescent excitations‡ of pure iodine vapour where it is unaccompanied by 3460–3015 Å system. A probable explanation for this continuum, as pointed out by Venkateswarlu,[26] is that it involves transitions between an upper stable state at 51528 cm.$^{-1}$ and a lower repulsive state dissociating into $^2P_{\frac{1}{2}} + {}^2P_{3/2}$ iodine atoms.

In order to determine the relation of the P-R bands to the emission bands in the region 3460–3015 Å together with the relation of the Skorko bands and P-R and K-M bands to one another it is necessary for one to obtain systematically the experimental data in the region 3500–1950 Å, using different temperatures ranging from room temperature to 1150° C. It will be also necessary to take juxtaposed spectra of the emission and absorption. At the present stage it appears likely that the Skorko bands may belong to the same system as the emission bands in the region 3460–3015 Å. If this correspondence is proved finally to be correct, the occurrence of the Skorko bands in absorption can be understood on the basis that at very high temperatures the $^3\Pi_u$ (O_u^+) state responsible for the Skorko bands is reached by the recombination of the $^2P_{3/2} + {}^2P_{\frac{1}{2}}$ iodine atoms which are present because of the thermal dissociation.§ This is supported by the fact that at high temperatures Uchida,[27] Wood[28] and others have obtained in thermal luminiscence the visible discrete bands of iodine which could be explained only on the supposition that the initial state of the bands is reached by the recombination of the $^2P_{3/2} + {}^2P_{\frac{1}{2}}$ atoms.

The So-called "Continuum" at 4300 Å

Elliott[9] and recently Methieson and Rees[15] refer to a continuum at 4300 Å obtained by electrical and fluorescent excitation of iodine vapour as

‡ The presence of the coutinuum in fluorescence of iodine vapour without the presence of foreign gases is indicated by the data of McLennan[5] as well as those of Rao and Rao.[8] It had been wrongly pointed out by Mathieson and Rees[15] that the continuum does not come in without the presence of foreign gas.

§ A similar explanation was given by Venkateswarlu[26] for the occurrence of the continua as 3413 Å and 3263 Å in absorption at high temperature.

involving the same transition as the band system 4420–4000 Å. The spectrum of iodine in the region 4525–3969 Å as obtained by exciting iodine vapour with a high frequency discharge was shown by Venkateswarlu in Fig. (*a*) of Plate XXV of his paper.[1] The spectrum was taken on a three-prism Steinheil glass spectrograph and the details are practically the same as those obtained earlier by Asagoe and Inuzuka.[29] The so-called continuum at 4300 Å is not a continuum but a group of five diffuse bands with intensity maxima at 4356·4, 4317·8, 4282·3, 4242·5 and 4201·8 Å giving an average mutual separation of 211 cm.$^{-1}$ among the constituent bands. The upper state of this group of diffuse bands will most probably be a state with a vibrational frequency of about 211 cm.$^{-1}$ and cannot be identical with the upper state of the band system 4420–4000 Å which has a vibrational frequency of 102 cm.$^{-1}$ A probable explanation for this group of diffuse bands as given by Venkateswarlu is that it arises in a transition from stable state at 51526 cm.$^{-1}$ with $\omega_0 \sim 215$ cm.$^{-1}$ to a repulsive state dissociating into $^2P_{\frac{1}{2}} + {}^2P_{\frac{1}{2}}$ iodine atoms. The potential energy curve of the lower state is probably nearly flat so that the constituent bands in the group are very well separated and their mutual separation gives the frequency of the upper state.

THE ELECTRONIC TRANSITIONS INVOLVED FOR THE DIFFERENT BAND SYSTEMS IN EMISSION DISCUSSED ABOVE

The band systems in the region 4420–4000 Å and 3460–3015 Å have a common lower level which is the $\sigma^2{}_g\pi^4{}_u\pi^3{}_g\sigma_u{}^3\Pi_u$ (O_u^+) level at $T_e = 15642$ cm.$^{-1}$ The upper states of these systems are at $T_e = 41411$ cm.$^{-1}$ and $T_e = 45937$ cm.$^{-1}$ respectively. On analogy with the corresponding band systems of bromine in the regions 3150–2970 Å and 2950–2670 Å discussed by Venkateswarlu and Verma,[16, 20] one can tentatively assign

$$\sigma_g{}^2\pi_u{}^2\sigma_g{}^4\sigma_u{}^2\,{}^3\Sigma_g^- (O_g^+ \text{ or } 1_g) \text{ and } \sigma_g{}^2\pi_u{}^2\pi_g{}^4\sigma_u{}^2\,{}^1\Sigma_g^+ (O_g^+)$$

for the two levels at 41411 cm.$^{-1}$ and 45937 cm.$^{-1}$ respectively. It is interesting to note that the average position of these two levels arising from the configuration $\sigma_g{}^2\pi_u{}^2\pi_g{}^4\sigma_u{}^2$ is 5·4 e.v. in close agreement with the value of 5·6 e.v. estimated by Mulliken[30] for the average position of the $\sigma_g{}^2\pi_u{}^2\pi_g{}^4\sigma_u{}^1$ configuration.

The weak band system 2785–2731 Å is probably analogous to the weak system 2660–2590 Å of bromine discussed by Verma.[21] The lower state of the system is again the $\sigma_g{}^2\pi_u{}^4\pi_g{}^3\sigma_u\,{}^3\Pi_u$ (O_u^+) level at 15642 cm.$^{-1}$ The discussion given by Verma about the different probable upper electronic terms for the upper state of the bromine system 2660–2590 Å is applicable also for the upper state of the iodine system 2785–2731 Å.

The lower state of the system 2730–2486 Å is the ground state of the molecule. The upper state of the system is at $T_e = 47207$ cm.$^{-1}$ and it has to be an 'ungerade' state. According to the term scheme developed by Mulliken,[30] the electronic configuration that gives 'ungerade' states at about this height is $\sigma_g^2 \pi_u^3 \pi_g^3 \sigma_u^2$. The electronic terms that arises from this configuration are $^1\Sigma_u^+ (O_u^+)$, $^3\Sigma_u^- (O_u^+, 1_u)$, $^1\triangle u\ (2_u)$, $^3\Sigma_u^+ (1_u, O_u^-)$, $^1\Sigma_u^- (O_u^-)$ and $^3\triangle u\ (3_u, 2_u, 1_u)$ of which the last three are expected to dissociate into $^2P + {}^2P$ normal iodine atoms and therefore cannot correspond to the stable state at 47207 cm.$^{-1}$ Of the remaining three $^1\triangle u\ (2_u)$ cannot combine with the ground state, and therefore the electronic term for the upper state of the system 2730–2486 Å is either $^1\Sigma_u^+ (O_u^+)$ or $^3\Sigma_u^- (O_u^+$ or $1_u)$.

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References

1. Venkateswarlu, P. .. *Proc. Ind. Acad. Sci.*, 1946, **24 A**, 480.
2. ———— .. *Ibid.*, 1947, **25 A**, 119.
3. ———— .. *Ibid.*, 1947, **25 A**, 133.
4. Asundi, R. K. and Venkateswarlu, P. *Ind. Jour. Phys.*, 1947, **21**, 101.
5. McLennan, J. C. .. *Proc. Roy. Soc.*, 1913, **88 A**, 289; 1915, **91 A**, 23.
6. Oldenberg, O. .. *Zs.f. Phys.*, 1923, **18**, 1.
7. Wood, R. W. .. *Physical Optics* (Macmillan, New York), 1946.
8. Rao, C. V. N. and Rao, V. R. *Ind. Jour. Phys.*, 1954, **28**, 403.
9. Elliott, A. .. *Proc. Roy. Soc., London*, 1940, **174 A**, 273.
10. Waser, J. and Wieland, K. .. *Nature*, 1947, **160**, 643.
11. Venkateswarlu, P. .. *Phys. Rev.*, 1951, **81**, 821.
12. Rank, D. H. .. *J. Opt. Soc. Am.*, 1946, **36**, 239.
13. ———— and Baldwin, W. M. *J. Chem. Phys.*, 1951, **19**, 1210.
14. Wieland, K. and Waser, J. .. *Phys. Rev.*, 1952, **85**, 385.
15. Mathieson, L. and Rees, A. L. G. *J. Chem. Phys.*, 1956, **25**, 753.
16. Venkateswarlu, P. and Verma, R. D. *Proc. Ind. Acad. Sci.*, 1957, **46 A**, 251.

17. Skorko, E. .. *Nature*, 1933, **131**, 366.

18. Herzberg, G. .. *Spectra of Diatomic Molecules* (D. VanNostrand Co., New York), 1950.

19. Brown, W. G. .. *Phys. Rev.*, 1931, **38**, 709.

20. Venkateswarlu, P. and Verma, R. D. *Proc. Ind. Acad. Sci.*, 1957, **46**, 416.

21. Verma, R. D. .. *Ibid.*, 1958, **47**, 196.

22. Private communication from Prof. Rank to Dr. P. Venkateswarlu

23. Pringsheim, P. and Rosen, B. .. *Z. Physik.*, 1928, **50**, 1.

24. Kimura, M. and Miyanishi, M. *Sci. Papers Inst. Phys. Chem. Res.* (*Tokyo*), 1929, **10**, 33.

25. Warren, D. T. .. *Phys. Rev.*, 1935, **47**, 1.

26. Venkateswarlu, P. .. *Ind. Jour. Phys.*, 1947, **21**, 43.

27. Uchida, Y. .. *Sci. Papers Inst. Phys. Chem. Res.*, 1936, **30**, 71.

28. Wood, R. W. .. *Phil. Mag.*, 1906, **12** (6), 324.

29. Asagoe, K. and Inuzuka, Y. .. *Sci. Rep., Tokyo, Burnika, Daigaku*, 1934, **2 A**, 73.

30. Mulliken, R. S. .. *Phys. Rev.*, 1934, **46**, 549.

31. Venkateswarlu, P. .. *Proc. Ind. Acad. Sci.*, 1947, **25 A**, 138.

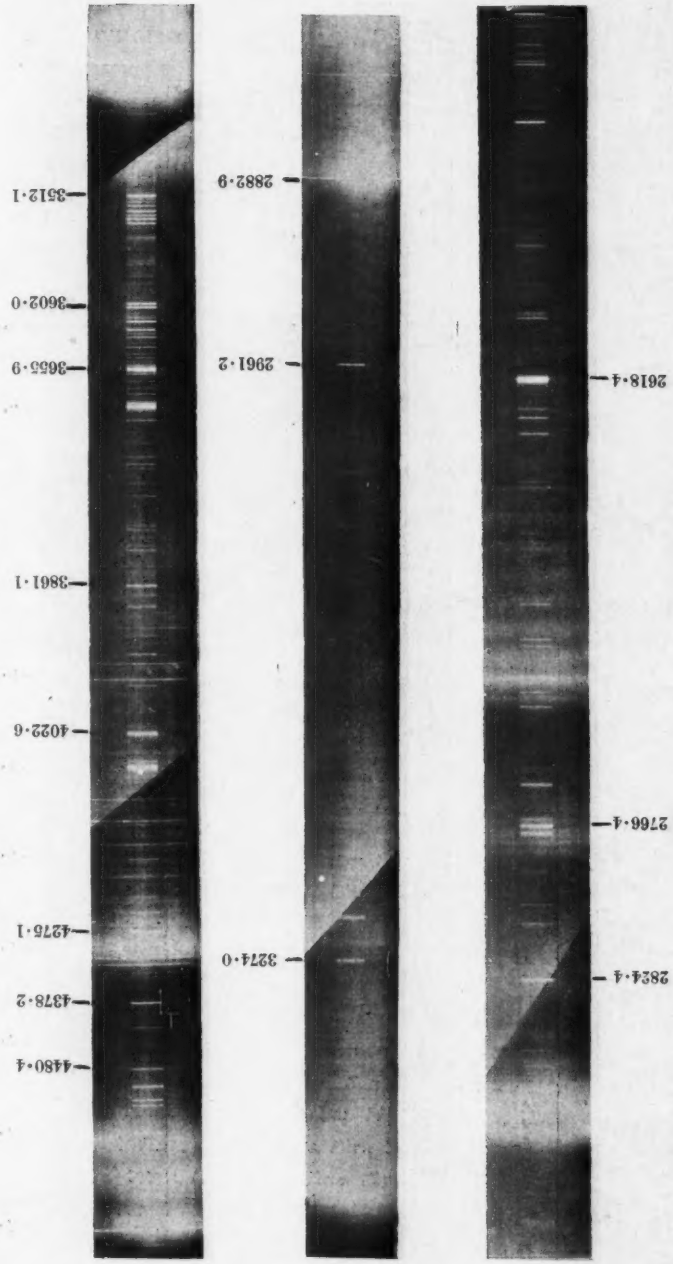

FIG. 1. The enlargement of the spectrum of I_2 excited in the presence of argon taken with a Hilger E_1 Littrow quartz spectrograph in the region λ 4800–2500 Å.

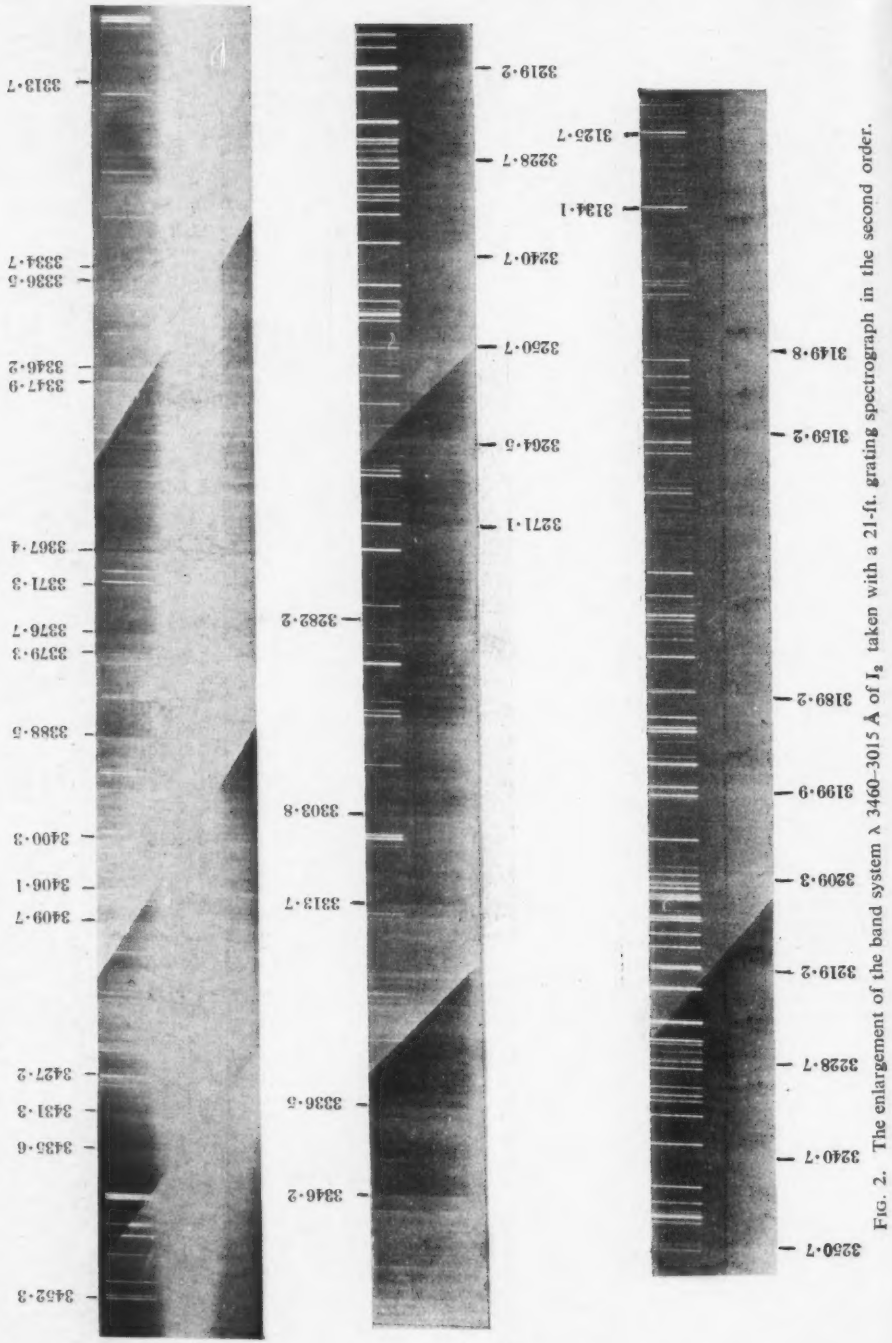

FIG. 2. The enlargement of the band system λ 3460–3015 Å of I_2 taken with a 21-ft. grating spectrograph in the second order.

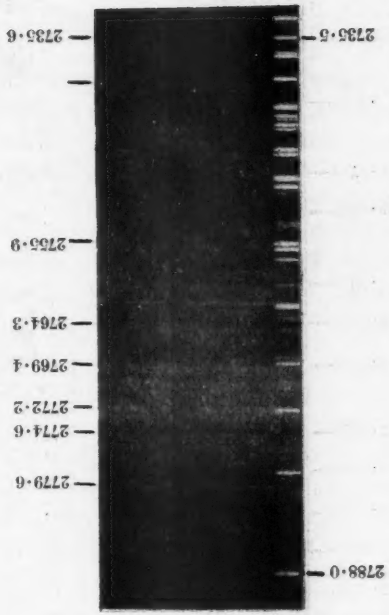

FIG. 3. The enlargement of the band system λ 2785–2731 Å of I_2 taken with a 21-ft. grating spectrograph in the first order.

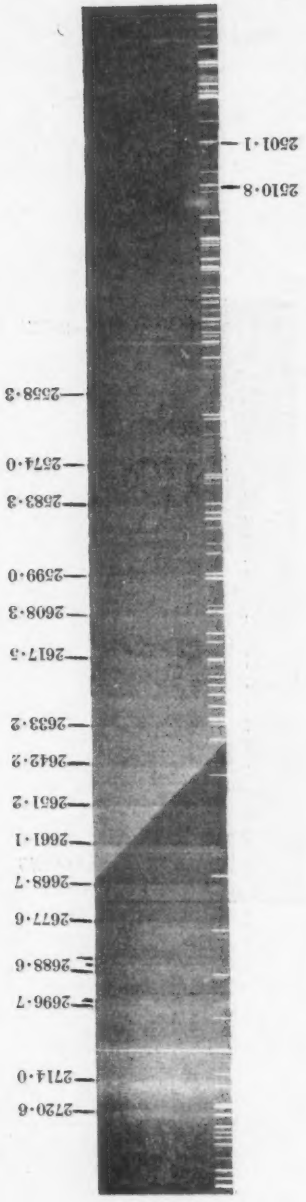

FIG. 4. The enlargement of the band system λ 2730–2486 Å taken with a 21-ft. grating spectrograph in the first order.

LIGHT PROPAGATION IN ABSORBING CRYSTALS POSSESSING OPTICAL ACTIVITY—ELECTROMAGNETIC THEORY

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§ 1. Introduction

In the present paper we shall give the electromagnetic theory of light propagation in absorbing crystals possessing optical activity: the theoretical presentation is a straightforward extension of that previously adopted for transparent active crystals.[1] We shall find that the results of the electromagnetic theory are, for most practical purposes, the same as obtained previously[2] on the basis of a simpler physical idea, *viz.*, by a 'method of superposition'—the results of which have been confirmed by detailed observations on the interesting phenomena displayed by amethyst.[3]

A complete solution of the electromagnetic theory of light propagation in absorbing active crystals has thus far been presented only for the case of uniaxial media.[4] Recently an entirely new and general method of formally solving the electromagnetic equations has been introduced by Jones[5] in a paper dealing with light propagation in anisotropic media (*see*, however, Appendix). We shall find in § 11, that it becomes essential to adopt this new method for solving the propagation of light along certain remarkable directions, *viz.*, the so-called *singular axes* which can exist both in active[3] as well as inactive[6,7] crystals.

§ 2. Formulation of the Problem

Consider an arbitrary direction of propagation Oz in the crystal—which direction we may conveniently take as being normal to the plane of the paper. Our problem is merely to determine the characteristic states of polarisation of the plane waves that can be propagated along this direction, as well as their velocities and absorption coefficients. The reason why only specific types of waves can be propagated along the z-direction is that the field vectors (in particular, the vectors **D** and **E**) of the electromagnetic wave are constrained to satisfy certain relations amongst them-

selves. Firstly they must satisfy Maxwell's equations; and secondly they must obey certain constitutive relations imposed by the properties of the medium, and which determine the optical characteristics of the medium. These latter relations will be determined by the polarisable characteristics of the medium, *i.e.*, the relation which the induced polarisation bears to the electric field of the light wave. (As is customary even in the case of transparent active crystals we shall assume for simplicity that there is no induced magnetization, *i.e.*, that $\mathbf{B} = \mathbf{H}$, though—as in that case—this assumption appears to violate energy considerations.)

§ 3. MAXWELL'S RELATIONS FOR A PLANE WAVE FIELD

Since we are interested in plane waves propagating in the z-direction, the field vectors do not vary over planes normal to the z-direction. If $\mathbf{k}$ denote a unit vector along the z-axis, we may use the operator $\mathbf{k}\,(\partial/\partial z)$ in place of the gradient operator ∇ in the Maxwell's equations—or rather in the standard relation obtained by eliminating $\mathbf{H}$ between the Maxwell's equations. The latter relations (*see, e.g.*, Page and Adams,[8] eq. 82–9) then assume the form

$$\ddot{\mathbf{D}} = c^2 \frac{\partial^2}{\partial z^2} [\mathbf{E} - \mathbf{k}\,(\mathbf{k} \cdot \mathbf{E})]. \tag{1}$$

The components of this equation take the simpler form

$$\ddot{\mathrm{D}}_x = c^2 \frac{\partial^2 \mathrm{E}_x}{\partial z^2}\,; \qquad \ddot{\mathrm{D}}_y = c^2 \frac{\partial^2 \mathrm{E}_y}{\partial z^2} \tag{2}$$

$$\ddot{\mathrm{D}}_z = 0. \tag{3}$$

The last condition implies the transversality of the displacement vector—since we shall be concerned only with fields varying harmonically in time. Also we shall first restrict our consideration to homogeneously polarised plane waves, so that

$$\mathbf{D},\ \mathbf{E} \sim \exp.\ i\omega \left(t - \frac{z}{c} \cdot \bar{n}\right) \times \mathbf{D}_0,\ \mathbf{E}_0 \tag{4}$$

where n is the complex refractive index. Under these conditions the operation $\partial/\partial z$ becomes identical with multiplication by $-i\omega\bar{n}/c$ and the operation $\partial/\partial t$ with multiplication by $i\omega$. Thus for a plane wave field of type (4) Maxwell's equations (with $\mathbf{H}$ eliminated) finally assume the elegant form

$$\bar{v}^2 \mathrm{D}_x = c^2 \mathrm{E}_x\,; \qquad \bar{v}^2 \mathrm{D}_y = c^2 \mathrm{E}_y \tag{5}$$

where $\bar{v}$ represents the complex velocity $c/\bar{n}$ of the damped wave.

§ 4. Properties of the Medium

The dielectric displacement in the medium depends on the electric vector, and, for a transparent optically active crystal,[9] **D** may be expressed as an explicit vector function of **E** by the use of the dielectric tensor (ϵ) and gyration tensor (g); it was shown in a previous paper[1] that it was more convenient to reverse the procedure and express **E** as an explicit function of **D** by the use of the index-tensor (a), and a modified gyration tensor (γ). When we turn to media possessing absorption, the components of the dielectric tensor and the gyration tensor will become complex quantities: in terms of our modified presentation it may be shown that the consequence of this is that the constants of the index tensor and the modified gyration tensor have to be replaced by complex quantities (*see* Appendix). Thus the relation between **E** and **D** may be expressed in the same form as previously given for transparent active crystals (reference 1, eq. 2 *a*).

$$c^2\mathbf{E} = (\bar{a})\,\mathbf{D} - i\bar{\Gamma} \times \mathbf{D}. \tag{6}$$

Here $(\bar{a})$ is a symmetric tensor—the complex index-tensor; and $\bar{\Gamma}$ is an auxiliary vector which depends on the direction of the wave-normal **s**, being given by

$$\bar{\Gamma} = (\bar{\gamma})\,\mathbf{s} \tag{7}$$

where $(\bar{\gamma})$ represents the 'tensor of optical activity'—a general tensor with complex components. It is convenient to express the above relations in terms of tensors having real components; *these tensors will in turn separately determine the various optical characteristics of the medium.*

Thus in (6) and (7) we may substitute

$$(\bar{a}) = (a) + i\,(b) \tag{8}$$

$$(\gamma) = (\gamma)_3' + i\,(\gamma'). \tag{9}$$

Here (a) and (b) are the usual index- and absorption-tensors which occur for example in optically inactive absorbing crystals, and which define the *index-* and *absorption-ellipsoids*; (γ) is the tensor of optical rotation which was referred to in our paper on transparent active crystals[1] as the modified gyration tensor. The new tensor (γ') may be called the tensor of circular

dichroism for reasons which will become apparent as we proceed. In eq. (6) it is clear that we may further substitute

$$\bar{\Gamma} = \Gamma + i\Gamma' \tag{10}$$

where

$$\Gamma = (\gamma)\,\mathbf{s} \tag{11}$$

$$\Gamma' = (\gamma')\,\mathbf{s}. \tag{12}$$

§ 5. Solution of the Electromagnetic Equations

We now write down the x and y components of the vector equation (6) after expanding the cross-product and omitting terms in D_z (since the latter is equal to zero).

$$\left.\begin{aligned} c^2\mathrm{E}_x &= \bar{a}_{11}\mathrm{D}_x + (\bar{a}_{12} + i\bar{\Gamma}_z)\,\mathrm{D}_y \\ c^2\mathrm{E}_y &= (\bar{a}_{12} - i\bar{\Gamma}_z)\,\mathrm{D}_x + \bar{a}_{22}\mathrm{D}_y \end{aligned}\right\}. \tag{13}$$

Substituting for $c^2\mathrm{E}_x$ and $c^2\mathrm{E}_y$ from (5) we obtain as our fundamental equations:

$$\left.\begin{aligned} \bar{v}^2 - \bar{a}_{11} &= (\bar{a}_{12} + i\bar{\Gamma}_z)\left(\frac{\mathrm{D}_y}{\mathrm{D}_x}\right) \\ \bar{v}^2 - \bar{a}_{22} &= (\bar{a}_{12} - i\bar{\Gamma}_z)\left(\frac{\mathrm{D}_x}{\mathrm{D}_y}\right) \end{aligned}\right\}. \tag{14}$$

In general there will be two pairs of roots $\bar{v}_a$, $(\mathrm{D}_y/\mathrm{D}_x)_a$ and $\bar{v}_b$ $(\mathrm{D}_y/\mathrm{D}_x)_b$ which will satisfy these simultaneous equations. These will give the complex velocities and states of polarisation of the two waves that can be propagated in the z-direction. If we multiply the two equations of (14) to eliminate $(\mathrm{D}_y/\mathrm{D}_x)$ we obtain the following quadratic in $\bar{v}^2$ whose roots $\bar{v}_a{}^2$ and $\bar{v}_b{}^2$ determine the complex velocities (*i.e.*, the velocities and absorption coefficients of the waves):

$$(\bar{v}^2 - \bar{a}_{11})(\bar{v}^2 - \bar{a}_{22}) = \bar{a}_{12}{}^2 + \bar{\Gamma}_z{}^2. \tag{15}$$

Subtracting the second equation of (14) from the first to eliminate $\bar{v}^2$, we get

$$(\bar{a}_{12} + i\bar{\Gamma}_z)\left(\frac{\mathrm{D}_y}{\mathrm{D}_x}\right) - (\bar{a}_{12} - i\bar{\Gamma}_z)\left(\frac{\mathrm{D}_x}{\mathrm{D}_y}\right) = -(\bar{a}_{11} - \bar{a}_{22}).$$

Or,

$$(\bar{a}_{12} + i\bar{\Gamma}_z)\left(\frac{\mathrm{D}_y}{\mathrm{D}_x}\right)^2 + (\bar{a}_{11} - \bar{a}_{22})\left(\frac{\mathrm{D}_y}{\mathrm{D}_x}\right) - (\bar{a}_{12} - i\bar{\Gamma}_z) = 0. \tag{16}$$

This is a quadratic in (D_y/D_x) and *its roots specify the states of polarisation of the waves.* Since these roots will in general be complex, the waves will be elliptically polarised.

The task of discussing in greater detail the velocities, absorption coefficients and states of polarisation of the waves is complicated by the fact that all the coefficients occurring in (15) and (16) are really complex quantities:

$$\bar{a}_{hk} = a_{hk} + ib_{hk}\ ;\quad \bar{\Gamma}_z = \Gamma_z + i\Gamma_z'. \tag{17}$$

It is worthwhile pointing out that the a_{hk} and b_{hk} (which are the components of the index and absorption tensors respectively) are also the constants occurring in the equation to the elliptic sections of the index- and absorption-ellipsoids by the xy plane; in other words the equation to these elliptic sections are respectively

$$\left.\begin{aligned} a_{11}x^2 + a_{22}y^2 + 2a_{12}xy &= 1 \\ b_{11}x^2 + b_{22}y^2 + 2b_{12}xy &= 1 \end{aligned}\right\}. \tag{18}$$

Also Γ_z is the scalar parameter of optical rotation already met with in the case of transparent optically active crystals[1]; whilst Γ_z' may be called the scalar parameter of circular dichroism for reasons which will be discussed in the next section.

§ 6. Circular Dichroism and Its Directional Variation

The characteristic effect introduced by the presence of the parameter Γ_z' may be best revealed by supposing linear birefringence and linear dichroism to be absent, *i.e.*, by setting [in equations (15) and (16)],

$$a_{11} = a_{22} = a;\quad a_{12} = 0;\quad b_{11} = b_{22} = b;\quad b_{12} = 0$$

i.e.,

$$\bar{a}_{11} = \bar{a}_{22} = \bar{a};\quad \bar{a}_{12} = 0.$$

Such a situation actually occurs for a direction of propagation along the uniaxial axis in a crystal of uniaxial symmetry, since the sections of the index- and absorption-ellipsoids will be circular. Equations (16) and (15) then yield

$$\frac{D_y}{D_x} = \pm i;\quad v^2 = \bar{a} \mp \bar{\Gamma}_z. \tag{19}$$

This means that the waves are right and left circularly polarised and if $\bar{v}_r$ and v_l be the complex velocities of the circularly polarised waves, then

$$\bar{v}_l^2 - \bar{v}_r^2 = 2\bar{\Gamma}_z. \tag{20}$$

The complex velocity $\bar{v}$ is related to the actual velocity v and the extinction coefficient κ by the usual relation

$$\bar{v} = \frac{c}{n - i\kappa} = v\left(1 + \frac{i\kappa v}{c}\right) \tag{21}$$

the terms containing the square of the extinction coefficient being negligible in magnitude. Introducing this in equation (20), we obtain to a high degree of approximation

$$n_r - n_l = \Gamma_z \cdot \frac{c}{{v_m}^3} = \rho_0 \tag{22}$$

$$\kappa_l - \kappa_r = \Gamma_z' \cdot \frac{c}{{v_m}^3} = \sigma_0 \tag{23}$$

where v_m is a mean velocity.

It will now be clear why Γ_z and Γ_z' may be referred to as the parameters of optical rotation and circular dichroism corresponding to the direction of propagation z. The values of these parameters for a general direction of propagation s may be denoted by Γ_s and Γ_s'. The parameter of optical rotation has been shown to be a quadratic function of the direction cosines of propagation by virtue of (11) (*see* ref. 1, § 6); the same statement must therefore be true for the directional variation of the parameter of circular dichroism. If we lay off two radii vectores r_1 and r_2 parallel to the direction of propagation such that their lengths are given by

$$\frac{1}{{r_1}^2} = |\Gamma_s| = \rho_0 \cdot \frac{{v_m}^3}{c} \tag{24}$$

$$\frac{1}{{r_2}^2} = |\Gamma_s'| = \sigma_0 \frac{{v_m}^3}{c} \tag{25}$$

then (24) and (25) define respectively a surface of optical rotation and a surface of circular dichroism. Given these surfaces we may determine Γ_s and Γ_s' for any direction of propagation, or alternatively the coefficients of circular birefringence and circular dichroism (ρ_0 and σ_0) for any direction.* (The sign to be attached may be supposed to be marked on the surface.)

§ 7. Analytical Presentation of the Method of Superposition

The states of polarisation of the waves propagated along any direction as well as their velocities and absorption coefficients may in principle be

* We take the mean velocity v_m for the direction in question to be given by equation (14) of reference 6.

obtained from equations (15) and (16). In practice, in order to be able to study the variation of these properties with direction the results would have to be cast into a simpler parametrical form—as Voigt[10] was compelled to do even in the case of inactive absorbing crystals. Now the propagation in an absorbing active crystal has been previously analysed without using the electromagnetic theory, by a method of superposition; this method, *when developed by the use of the Poincaré sphere*, leads to results which are automatically in such a parametrical form, and we shall show in the next section that these results can be modified so as to represent accurately the results of the electromagnetic theory. Unfortunately the modifications necessary can be perceived only if the results of the method of superposition, instead of being expressed in simple parametrical form, are expressed analytically by equations formally similar to those of the electromagnetic theory. For this purpose we shall in this section develop the consequences of the superposition method not by the geometrical methods of our previous paper,[2] but by analytical methods, along the lines followed by Jones[11,12] who has adopted a matrix calculus treatment.

A detailed physical description of the method of superposition may be found in references 6 and 2. Let $\vec{D}$ be the vibration at the plane z in the crystal.† The vibration which would obtain at the plane $(z + dz)$ if the crystal were transparent and inactive may be represented by $\vec{D} + \partial_1\vec{D}$. This vibration may be obtained by multiplying the components of $\vec{D}$ along the principal planes of linear birefringence Ox' and Oy' by the factors

$$\exp.\left(-i\frac{2\pi}{\lambda_0}n_1 dz\right)$$

and

$$\exp.\left(-i\frac{2\pi}{\lambda_0}\cdot n_2 dz\right) \text{ respectively.}$$

Then

$$\left.\begin{aligned}\partial_1 D_{x'} &= -i\frac{2\pi}{\lambda_0}n_1 D_{x'}\\ \partial_1 D_{y'} &= -i\frac{2\pi}{\lambda_0}n_2 D_{y'}\end{aligned}\right\}. \tag{26}$$

† The displacement vector is here written as a two-dimensional vector since it lies on the wavefront. Also the vibration is taken as $\vec{D}e^{i\omega t}$, *i.e.*, in the present section the time factor is not included within the symbol for the displacement vector, which is therefore only a function of z.

This may be written symbolically as

$$\partial_1 \vec{D} = -i \frac{2\pi}{\lambda_0} dz\, [n]\, \vec{D}. \tag{27}$$

where $[n]$ represents a symmetric 2×2 matrix or tensor operator whose principal directions coincide with the principal planes of linear birefringence and whose principal values are n_1 and n_2—determined from an index-ellipsoid as for a transparent inactive crsytal.

Similarly let $\partial_2 \vec{D}$ represent the partial increment to the initial vibration $\vec{D}$ when subjected to the infinitesimal operation of linear dichroism (corresponding to the thickness dz). Then we will have

$$\partial_2 \vec{D} = -\frac{2\pi}{\lambda_0} dz\, [\kappa]\, \vec{D} \tag{28}$$

where $[\kappa]$ represents a symmetric tensor whose principal directions coincide with the principal planes of linear dichroism and whose principal values are κ_1 and κ_2 as given by an absorption ellipsoid [*see* eq. (12) of ref. 6].

Under the combined effects of linear birefringence and linear dichroism the partial increment $\partial' \vec{D}$ to the initial vibration $\vec{D}$ may be obtained by adding (27) and (28). We may then write

$$\partial' \vec{D} = -i \frac{2\pi}{\lambda_0} dz\, [\bar{n}]\, \vec{D} \tag{29}$$

the components of the symmetric tensor $[\bar{n}]$ being given by

$$\bar{n}_{ij} = n_{ij} - i\kappa_{ij} \tag{30}$$

where the n_{ij} and κ_{ij} are the components of $[n]$ and $[\kappa]$ respectively.

Thus the state of vibration $\vec{D} + \partial' \vec{D}$ at the plane $z + dz$ for an *inactive* absorbing crystal is given by writing equation (29) in full:

$$\left.\begin{aligned} \partial' D_x &= -i \frac{2\pi}{\lambda_0} dz\, (\bar{n}_{11} D_x + \bar{n}_{12} D_y) \\ \partial' D_y &= -i \frac{2\pi}{\lambda_0} dz\, (\bar{n}_{12} D_x + \bar{n}_{22} D_y) \end{aligned}\right\}. \tag{31}$$

These equations correspond to eq. (29) of reference 6; the $\bar{n}_{ij}$ have the same significance as in that paper and are determined from the sections to the index- and absorption-ellipsoids.

Let $(\vec{D} + \partial_3\vec{D})$ represent the vibration obtained by subjecting the vibration $\vec{D}$ to the infinitesimal operation of rotation through an anticlockwise angle ρdz—where $\rho\ (\equiv \rho_0\pi/\lambda_0)$ is the optical rotatory power for the direction z as determined from a surface of optical rotation according to equation (24). Then

$$\left.\begin{aligned} D_x + \partial_3 D_x &= D_x - \frac{\pi}{\lambda_0}\rho_0 dz . D_y \\ D_y + \partial_3 D_y &= \frac{\pi}{\lambda_0}\rho_0 dz D_x + D_y \end{aligned}\right\}. \tag{32}$$

It remains to consider the partial increment $\partial_4\vec{D}$ due to the operation of circular dichroism (corresponding to the passage dz): this operation consists in resolving the initial vibration $\vec{D}$ into its left and right circular components and multiplying the amplitudes of these components by $(1 - \pi/\lambda_0 \cdot \sigma_0 dz)$ and $(1 + \pi/\lambda_0 \cdot \sigma_0 dz)$; σ_0 is the coefficient of circular dichroism (corresponding to the difference in the extinction coefficients of the circularly polarised components) as obtained from a surface of circular dichroism according to equation (25). Clearly this operation differs from the operation of optical rotation (regarded as circular birefringence) *only in that the constant* $i\sigma_0$ *occurs in place of* ρ_0. Let $\partial''\vec{D}$ represent the partial increment to the initial vibration $\vec{D}$ due to the combined effects of optical rotation and circular dichroism (for the thickness dz). Then according to what has been said above $\partial''\vec{D}$ will be given by an expression which is similar to the expression for $\partial_3\vec{D}$ [which may be written down from equation (32)] except for the following difference: the constant ρ_0 will have to be replaced by $\bar{\rho}$ where

$$\bar{\rho} = \rho_0 + i\sigma_0. \tag{33}$$

In other words we will have

$$\left.\begin{aligned} \partial'' D_x &= -\frac{\pi}{\lambda_0} dz \cdot \bar{\rho} D_y \\ \partial'' D_y &= +\frac{\pi}{\lambda_0} \cdot dz \cdot \bar{\rho} D_x \end{aligned}\right\}. \tag{34}$$

If $\vec{D} + d\vec{D}$ represents the vibration at the plane $z + dz$ in the optically active absorbing crystal then $d\vec{D}$ represents the total increment to the initial

vibration $\vec{D}$ under the combined effect of all the operations mentioned above. Thus $d\vec{D}$ is given by adding (31) and (34):

$$\left.\begin{aligned} dD_x &= -i\frac{2\pi}{\lambda_0}dz\,\{\bar{n}_{11}D_x + (\bar{n}_{12} - \tfrac{1}{2}i\bar{\rho})\,D_y\} \\ dD_y &= -i\frac{2\pi}{\lambda_0}dz\,\{(\bar{n}_{12} + \tfrac{1}{2}i\bar{\rho})\,D_x + n_{22}D_y\} \end{aligned}\right\}. \tag{35}$$

We wish to determine the *particular* states of polarisation of $\vec{D}$ for which the vibration is propagated unchanged with a specific complex velocity. From equation (14) we see that for such a disturbance we have

$$d\vec{D} = -i\frac{2\pi}{\lambda_0}dz\,.\,\bar{n}\vec{D} \tag{36}$$

Writing down the x and y components of (36) and comparing with (35) we finally obtain

$$\left.\begin{aligned} \bar{n} - \bar{n}_{11} &= (\bar{n}_{12} - \tfrac{1}{2}i\bar{\rho})\frac{D_y}{D_x} \\ \bar{n} - \bar{n}_{22} &= (\bar{n}_{12} + \tfrac{1}{2}i\bar{\rho})\frac{D_x}{D_y} \end{aligned}\right\} \tag{37}$$

which determine the characteristic states of polarisation D_y/D_x of the waves and their complex refractive indices $\bar{n}$—according to the method of superposition.

§ 8. Simplification of the Results of the Electromagnetic Theory

The equations (37) deduced by the superposition method are formally similar to the equations (14) deduced by the electromagnetic theory. It may be shown that the quadratic equation for D_y/D_x which may be obtained from (37) will have coefficients proportional to the corresponding coefficients in equation (16)—the factor of proportionality being $(-c/2v_m{}^3)$. It follows that the states of polarisation of the waves as obtained by the electromagnetic theory are *identical* with those obtained by the superposition method. Hence the points representing these states of polarisation on the Poincaré sphere‡ may be determined exactly as described in ref. 2—the parameters (ϕ, ψ) which specify the states of polarisation being the same in both methods.

‡ The Poincaré sphere merely represents a method of mapping states of polarisation, and hence need not be used only in conjunction with methods of superposition.

In the second place, *because of the formal similarity between equations* (37) *and* (14), it is clear that for every equation derived by the method of superposition a corresponding equation obtainable from the electromagnetic theory may be written down by inspection—merely by replacing the symbols according to a scheme which transforms (37) to (14). In addition to the replacement scheme already used for this purpose in inactive absorbing crystals (ref. 6, § 8), we have only to add that the symbols ρ_0 and σ_0 have to be replaced $-2\Gamma_z$ and $-2\Gamma_z'$ respectively. Simple expressions for the refractive indices and absorption coefficients of the waves have been derived in ref. 2, § 9 *c*, by the superposition method (using the Poincaré sphere). The corresponding equations from the electromagnetic theory will be:

$$v^2 = \tfrac{1}{2}(a_1 + a_2) + \tfrac{1}{2}\sqrt{(a_1 - a_2)^2 + (2\Gamma_z)^2} \cdot \cos 2\phi. \tag{38}$$

$$\kappa \cdot \frac{2v^3}{c} = \tfrac{1}{2}(b_1 + b_2) + \tfrac{1}{2}\sqrt{(b_1 - b_2)^2 + (2\Gamma_z')^2} \cdot \cos 2\psi. \tag{39}$$

For directions of propagation not in the vicinity of an optic axis it can be shown (as in ref. 2, § 7) that the velocities and absorption coefficients of the waves may be determined from the index and absorption ellipsoids. It is only for directions in the vicinity of an optic axis that the complications caused by the ellipticity of the waves make their appearance; for such directions, since the birefringence is necessarily small, the difference between the above expressions and those given by the method of superposition will not in general be of any practical significance.

§ 9. The Singular Axes

Among the most remarkable of the properties of absorbing crystals—both inactive and active—is the possibility of the occurrence of so-called *singular axes*. A singular axis represents a direction for which the quadratic equation (16)—which determines the states of polarisation of the waves—has equal roots; the condition ($b^2 = 4ac$) under which this can obtain ensures at the same time the equality of the roots of the quadratic equation (15) which determines the velocities of the waves. Thus along a singular axis there is only *one* particular state of polarisation which can be propagated without change of form. In a previous paper[3] we have already discussed (with reference to the particular example of amethystine quartz) the following problems: the conditions under which it is possible for singular directions to exist in optically active crystals, the location of these axes, and the state of (elliptic) polarisation of the single wave that can be propagated along a singular axis. In the present paper, therefore, we confine ourselves to the following interesting query: what will happen when

a plane wave incident along a singular direction is in a state of polarisation *other* than that which *alone* can be propagated unchanged along that axis? In the particular case when the incident vibration is in a state of polarisation *orthogonal* to that of the wave which can be propagated unchanged along the singular axis, it had been supposed by Voigt[13] (in the case of inactive crystals) that the incident light would be totally reflected away, the reflection being partial in practical cases. That this is far from being the case has been shown experimentally by the author both in the case of iolite[7] (an optically inactive crystal) and amethyst[3] (an optically active crystal). The experimental results in the former case were readily explained[6] in detail (ref. 6, § 6 *b*) by a direct application of the method of superposition—according to which the incident vibration would obviously be propagated with a progressive change in its state of polarisation. *The same treatment and results apply* mutatis mutandis *to optically active absorbing crystals also.* Furthermore, it had been argued from considerations of continuity that the results given by the method of superposition could not really be contradictory to those of the electromagnetic theory. But how exactly the propagation of an arbitrary vibration along a singular axis could be directly handled by the electromagnetic theory was not apparent to the author till the publication of a recent paper by Jones[5]—in which is contained a new method of solving the electromagnetic equations in any anisotropic medium (transparent or absorbing). We present the method in a slightly modified form suitable for our present use.

§ 10. THE WAVE EQUATION FOR A PLANE WAVE PROPAGATED WITH CHANGE OF POLARISATION

In this section we wish to write down a suitable equation to represent a plane wave in a homogeneous medium, the wave being in general propagated with a progressive change in its state of polarisation. Firstly we shall take the vibration $\vec{D}$ at any plane z to be varying as $e^{i\omega t}$ so that

$$\frac{\partial \vec{D}}{\partial t} = i\frac{2\pi}{\lambda_0} \cdot c\vec{D}. \tag{40}$$

Here the displacement vector has been written as a two-dimensional vector $\vec{D}$ since it is entirely transversal to the wave according to (3). As for the dependance of $\vec{D}$ on z, the form of the equation to be assumed is immediately suggested by equations (31) and (35) of § 7. The vibration at the plane $z + dz$ may be taken to be a linear *vector* function of the vibration

at the plane z (at the same instant), since it is *not* assumed that both are necessarily in the same state of polarisation. We may then write

$$\frac{\partial \vec{D}}{\partial z} = -i\frac{2\pi}{\lambda_0}[n']\vec{D} \tag{41}$$

where $[n']$ is a two-by-two matrix operator. This resembles exactly the equation (36) which is satisfied by a usual plane wave of the form (4), but for the following difference: the refractive index $\bar{n}$ has been replaced by a 'refractive index tensor' $[n']$ in order that the same equation may represent a general plane wave propagated in a homogeneous anisotropic medium. This procedure is essentially in the same spirit as that of replacing the real refractive index by a complex quantity in order that the form of the usual equation to a plane wave in a transparent isotropic medium may still be retained to represent what is really a damped wave in an absorbing isotropic medium.

From (40) and (41), we obtain by differentiating with respect to t and z respectively

$$\frac{\partial^2 \vec{D}}{\partial t^2} = c^2[n']^{-2}\frac{\partial^2 \vec{D}}{\partial z^2}. \tag{42}$$

The above equation represents the wave equation satisfied by the disturbance propagated with change of polarisation; it resembles the usual form of the wave equation to a plane disturbance except that in place of the square of the velocity we have the matrix operator $c^2[n']^{-2}$.

As a simple example of a plane disturbance propagated with progressive change of polarisation we may remark that when a plane wave which is linearly polarised at a suitable azimuth is incident normally on a quarter-wave plate the incident linear vibration goes through progressive stages of elliptic polarisation and then emerges circularly polarised. This example also illustrates why, in usual cases, we need not directly seek general solutions representing disturbances propagated with change of polarisation: as will be evident in the example quoted, such a general solution is obtained by superposing the two characteristic plane wave solutions of the usual form (4)—*provided two such distinct solutions exist.*

§ 11. Second Method of Solving the Electromagnetic Equations

Our task is now to determine the refractive index tensor $[n']$ or alternatively the tensor $c^2[n']^{-2}$. The result is sufficiently elegant to be stated

straightaway. Just as in an isotropic medium we have $n^2 = \epsilon$, where ϵ is the dielectric constant, in the present case it will be shown that

$$[n']^2 = [\epsilon], \tag{43}$$

where $[\epsilon]$ is the two-by-two matrix connecting $\vec{D}$ and $\vec{E}$:

$$\vec{D} = [\epsilon]\,\vec{E}. \tag{44}$$

Here $\vec{E}$ represents the 'projection' of the electric vector on the wavefront, being thus defined by the x and y components of the actual electric vector.

To establish (44) we note that the Maxwell's equations (2) may be written as

$$\frac{\partial^2 \vec{D}}{\partial t^2} = c^2 \frac{\partial^2 \vec{E}}{\partial z^2}. \tag{45}$$

The properties of the medium can be expressed in the form

$$c^2 \vec{E} = [A]\,\vec{D} \tag{46}$$

where [A] is a two-by-two matrix whose components may be written down from equation (13).

From (45) and (46) we have

$$\frac{\partial^2 \vec{D}}{\partial t^2} = [A] \frac{\partial^2 \vec{D}}{\partial z^2}. \tag{47}$$

Comparing with (42) we find that whatever be the state of polarisation of $\vec{D}$ a solution of the form (41) is possible with

$$c^2\,[n']^{-2} = [A]. \tag{48}$$

This relation is equivalent to (43) as may be seen by comparing (44) and (46). Thus the refractive index matrix $[n']$ can be determined§ for any direction of propagation from the relation

$$[n'] = c\,[A]^{-\frac{1}{2}} \tag{49}$$

We may briefly refer to the connection between the present method of solving the electromagnetic equations and that adopted in § 5. Though the wave equation (42) in general describes a disturbance propagated with

§ Only the physically significant square root of $[A]^{-1}$ is to be taken. For this and other mathematical questions which arise in the representation by matrix methods *see* Jones.[5,12]

a progressive change of polarisation this is not always the case. It will obviously reduce to the customary wave equation (for a homogeneously polarised disturbance) for those *particular* states $\vec{D}$ which satisfy the relation

$$[A]\,\vec{D} = \bar{v}^2\vec{D} \tag{50}$$

the complex velocity of the wave being $\bar{v}$. It will now be seen that the equations (13), previously used in § 5, are really the components of this vector equation, and as is shown by the procedure adopted there—the above equation is *usually* satisfied for two states of $\vec{D}$ (the eigenvectors of the matrix A) with *two* corresponding values of v^2 (the eigenvalues of the matrix A). For these particular states of $\vec{D}$ the equation (41) must also reduce to the form (36), *i.e.*, in the terminology of matrix calculus, these states of $\vec{D}$ are also the eigenvectors of the refractive index tensor $[n']$, the corresponding eigenvalues being the complex refractive indices of the waves.

From what has been said above, it is clear that a singular axis represents a special direction for which the matrix A has only *one* eigenvector, and correspondingly only *one* eigenvalue. This does not *in principle* lead to any difficulty in determining the refractive index matrix $[n']$ from (49), though of course the peculiar properties of [A] mentioned above are also carried over to $[n']$. On the other hand, when we adopt the method of superposition the refractive index tensor $[n']$ is considered as the sum of four parts each of which (it is assumed) may be directly determined in a simple fashion from the four corresponding surfaces defining the optical properties of the media. Thus whether we adopt the superposition method or the electromagnetic theory, no special difficulty arises in determining the refractive index tensor $[n']$ for propagation along a so-called singular direction. Along a singular direction—as, indeed, along any other direction—we can have plane disturbances which are propagated with a progressive change of polarisation: the speciality about a singular direction is, however, that such a disturbance cannot in turn be regarded as the sum of two plane waves of constant polarisation—there being only *one* wave of the latter type.

The author owes a debt of gratitude to Prof. Sir C. V. Raman, at whose instance the initial experimental investigations on amethyst and iolite were undertaken by the author, and without whose encouragement the subsequent theoretical investigations on the properties of absorbing crystals would not have been possible.

§ 12. SUMMARY

The propagation of light along an arbitrary direction in an absorbing active crystal is solved by extending the treatment previously given[1] for transparent active crystals—the index tensor and the modified gyration tensor being replaced by corresponding tensors with complex components. The two waves are in general elliptically polarised, in states identical with those given by a method of superposition[2]; their velocities and absorption coefficients are likewise simple functions of the parameters which specify these states of polarisation on the Poincaré sphere.

Attention is drawn to the propagation along any singular direction (in active or inactive crystals) where only *one* homogeneously polarised plane wave solution is obtained—and not two. A more general theoretical approach[5] becomes necessary to establish—in agreement with experiment—that other solutions also exist, representing plane disturbances propagated with a progressive change of polarisation. For such a disturbance the wave equation satisfied by the displacement vector differs from the usual form only in that the square of the velocity has to be regarded as a tensor operator.

§ 13. REFERENCES

1. Pancharatnam .. *Proc. Ind. Acad. Sci.*, 1956, **43 A**, 247.
2. ———— .. *Ibid.*, 1957, **46 A**, 280.
3. ———— .. *Ibid.*, 1958, **47 A**, 201, 210.
4. Forsterling .. *Gottinger Nachr.*, 1912, p. 207.
5. Jones .. *J. Opt. Soc. Am.*, 1956, **46**, 126.
6. Pancharatnam .. *Proc. Ind. Acad. Sci.*, 1955, **42 A**, 86.
7. ———— .. *Ibid.*, 1955, **42 A**, 235.
8. Page and Adams .. *Electrodynamics*, Von Nostrand, 1949, Ch. 8.
9. Born .. *Optik*, Springer, 1933, p. 414.
10. Pockels .. *Lehrbuch der Kristalloptik*, Teubner, 1906, pp. 386–99.
11. Jones .. *J. Opt. Soc. Am.*, 1942, **32**, 486.
12. ———— .. *Ibid.*, 1948, **38**, 671.
13. Voigt .. *Ann. Physik.*, 1908, **27**, 1002.

APPENDIX

(*a*) *Derivation of the constitutive relation in the form* (6).—The relation between **D** and **E** for an optically active absorbing crystal may be written as

$$\mathbf{D} = (\epsilon)\,\mathbf{E} + \mathbf{P}_1 + \mathbf{P}_2. \tag{46}$$

The portion of the induced polarisation $\mathbf{P}_1$ contributes to the mean absorption and the linear dichroism, while $\mathbf{P}_2$ leads to optical rotatory power and circular dichroism. These are given by the expressions (*see* ref. 9):

$$\mathbf{P}_1 = -\,i\,(\epsilon')\,\mathbf{E}; \quad \mathbf{P}_2 = i\,\bar{\mathbf{G}} \times \mathbf{E}. \tag{47}$$

For usual values of absorption and optical activity $\mathbf{P}_1$ and $\mathbf{P}_2$ are so small that terms of the second order in $\mathbf{P}_1$ and $\mathbf{P}_2$ may be ignored. Hence to this degree of approximation $\mathbf{P}_1$ and $\mathbf{P}_2$ may be expressed as functions of **D** by substituting in (47) an approximate value of **E** obtained from (46), *viz.*, $\mathbf{E} = (\epsilon^{-1})\,\mathbf{D}$. We then obtain

$$\begin{aligned}(\epsilon)\,\mathbf{E} &= \mathbf{D} - \mathbf{P}_1 - \mathbf{P}_2 \\ &= \mathbf{D} + i\,(\epsilon'\epsilon^{-1})\,\mathbf{D} - i\,(\mathrm{R}\epsilon^{-1})\,\mathbf{D}\end{aligned}$$

where the operator $\bar{\mathbf{G}} \times$ is replaced by an antisymmetric matrix operator R (*see*, *e.g.*, ref. 8, eq. 85.2). We then obtain

$$\mathbf{E} = (\epsilon^{-1})\,\mathbf{D} + i\,(\epsilon^{-1}\epsilon'\epsilon^{-1})\,\mathbf{D} - i\,(\epsilon^{-1}\mathrm{R}\epsilon^{-1})\,\mathbf{D}. \tag{48}$$

If we choose axes of co-ordinates X, Y, Z along the principal axes of the dielectric tensor (ϵ) it can be shown by actual matrix multiplication that the operator $(\epsilon^{-1}\mathrm{R}\epsilon^{-1})$ is equal to the operator $1/c^2 \cdot \bar{\Gamma}\times$, where

$$\bar{\Gamma}_X = \frac{c^2}{\epsilon_Y \epsilon_Z} \cdot \bar{\mathrm{G}}_X; \quad \bar{\Gamma}_Y = \frac{c^2}{\epsilon_Z \epsilon_X} \cdot \bar{\mathrm{G}}_Y; \quad \bar{\Gamma}_Z = \frac{c^2}{\epsilon_X \epsilon_Y} \cdot \bar{\mathrm{G}}_Z. \tag{49}$$

Comparing (48) with (6) and (8) we see that the vector of optical activity $\bar{\Gamma}$ is given by the above equations, while the index and absorption tensors are given by

$$(a) = c^2\,(\epsilon^{-1}); \quad (b) = c^2\,(\epsilon^{-1}\epsilon'\epsilon^{-1}). \tag{50}$$

It must be remembered that $\bar{\mathbf{G}} = (\bar{g})\,\mathbf{s}$, where $(\bar{g})$ is the complex gyration tensor and **s** the wave-normal. If we write this relation in full (*see* ref. 9) it follows from (49) that the relation between the components of the tensor

of optical activity ($\bar{\gamma}$) and the components of the complex gyration tensor ($\bar{g}$) will be given by

$$\bar{\gamma}_{1m} = \frac{c^2}{\epsilon_Y \epsilon_Z} \cdot \bar{g}_{1m}; \quad \bar{\gamma}_{2m} = \frac{c^2}{\epsilon_Z \epsilon_X} \bar{g}_{2m}; \quad \bar{\gamma}_{3m} = \frac{c^2}{\epsilon_X \epsilon_Y} \cdot \bar{g}_{3m} \qquad (51)$$

$$(m = 1, 2, 3).$$

(*b*) *An error in Jones' paper.*—In a paper by Jones[5] dealing with propagation in anisotropic media, the constitutive relation between **D** and **E** for an optically active medium has been expressed in a form which has been thought to be equivalent to that given above [eqs. (46) and (47)] but is really quite different from it. In particular the term $\mathbf{P}_2$ in (47) has been assumed by Jones to be given by

$$\mathbf{P}_2 = \frac{c}{\omega} \{(\bar{g}) \nabla\} \times \mathbf{E} \qquad (52)$$

where ∇ is the gradient operator and ($\bar{g}$) the complex gyration tensor. That this relation is quite different from the customary form (47) may be easily seen in the particular case when we seek plane wave solution of the usual form (4) so that $\nabla = i\omega \bar{n}/c \cdot \mathbf{s}$. The relation (52) then becomes

$$\mathbf{P}_2 = i\bar{n} (\mathbf{G} \times \mathbf{E}). \qquad (53)$$

This is of course vitally different from the expression given in (47) since according to (53) the refractive index $\bar{n}$ which is one of the unknowns to be determined will itself be involved in the constitutive relations; more generally the refractive index tensor (n') will itself be involved in the matrix [A] occurring in (43). Accordingly, the relations given by Jones expressing his '**N**-matrix' in terms of the complex dielectric and gyration-tensors are in error.

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